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# TRANSACTIONS

OF THE

## ROYAL SOCIETY OF EDINBURGH.

VOL. XVI., PART IV., FOR THE SESSION 1847-1848.

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Plate X.,\* shewing the Parallel Roads of Glen-Roy, is given in illustration of MR MILNE'S Paper in Vol. XVI., Part III.







XXVIII.—*Memoir of Dr THOMAS CHARLES HOPE, late Professor of Chemistry in the University of Edinburgh.* By THOMAS STEWART TRAILL, M.D., F.R.S.E., Professor of Medical Jurisprudence in the University of Edinburgh.

(Read December 6, 1847.)

It is presumed that a notice of the life and labours of ONE, who was, for more than fifty years, a most skilful and successful teacher of chemistry in the Universities of Scotland, where he was the instructor of more than 15,500 pupils; who initiated in that interesting science many who now hear me; who long filled the office of vice-president amongst us, will not be unacceptable to the Royal Society of Edinburgh.

THOMAS CHARLES HOPE was a son of Dr JOHN HOPE, the first Regius Professor of Botany in the University of Edinburgh, and of JULIANA STEVENSON, daughter of an eminent physician in that city.

Professor JOHN HOPE was a grandson of Lord RANKEILLOR, an eminent Scottish judge in the early part of the last century, and son to Mr ROBERT HOPE, a respectable surgeon in Edinburgh. Professor HOPE died in 1786, at the age of 62. His family consisted of four sons and a daughter. ROBERT, the eldest, was bred to the bar, but died in early life; MARIANNE married JAMES WALKER, Esq., of Dalry, and died in 1837, leaving an only daughter, who became the wife of Sir JOHN WALL; JOHN, a Major in the army, who died in 1840; THOMAS CHARLES, the subject of this memoir, who was born on the 21st of July 1766, and died on the 13th of June 1844; JAMES, a writer to the Signet, who died in 1842, leaving several children.

THOMAS CHARLES, the third son of Dr JOHN HOPE, received the elements of his classical education in the High School of Edinburgh, to which he was sent in 1772; but in 1778 he was removed to a school at Dumfries, and was, 1779, entered as a student of general literature in this University, at the early age of thirteen; a practice still too common in this country. There he pursued the usual curriculum of general study, before he began to apply to medicine.

As was natural, he had devoted much attention to Botany, and, under his able father, had made such proficiency, that on the death of the latter in 1786, he aspired to the Botanical Chair; and, though supported by the influence of Sir JOSEPH BANKS, Sir GEORGE BAKER, and even by the favour of Royalty, the all-powerful influence of Mr DUNDAS prevailed, and he was unsuccessful. In June 1787, he obtained the degree of Doctor in Medicine at our University. Dr IRVINE, who held the Lectureship of Chemistry in the University of Glasgow, having died in the following month, Dr HOPE was appointed to fill the vacant chair, on





the 10th of October of the same year; and thus a new field was opened to his ambition.

It was no easy task with which young HOPE had to grapple. The Glasgow Lectureship had been successively held by men of consummate abilities, and high chemical acquirements. The immediate predecessors of Dr IRVINE, had been Dr ROBISON, Dr BLACK, and Dr CULLEN; men whose names will ever stand conspicuous in the science of Scotland. Instead of acting as a discouragement, this consideration only stimulated Dr HOPE to make every effort to prove himself no unworthy successor of these eminent teachers of chemical science. With the general doctrines of chemistry he was well acquainted; he possessed ingenuity in devising illustrative experiments, and a rare delicacy in chemical manipulation. Yet, as he has confessed to the writer of this memoir, from the shortness of the period for preparation, the scantiness of his apparatus, and the utter want of assistance in his laboratory, he regarded his first course of chemistry as very imperfect. But the novelty of his mode of teaching, and the neatness of his experiments, seem to have won the approbation of his auditory.

He was, at that period, a strenuous supporter of the then generally received doctrines of STAHL—that inflammable bodies owed that quality to the presence of a principle which was termed *phlogiston*, and of course taught that doctrine in this his first course of lectures. But his conversion to the Lavoisierian or French theory of chemistry was at hand.

It is generally known, that from 1777, LAVOISIER had doubted the existence of such a principle as *phlogiston*, and in 1785 proposed the antiphlogistic theory, supported by such facts and decisive experiments, that his views were speedily adopted by his own countrymen; though for a considerable time afterwards, they were not received in Britain.

The late Sir JAMES HALL happened to pass the winter of 1787 in Paris, and was much in the society of LAVOISIER, who showed great anxiety to make a convert of Sir JAMES, and, through him, to spread his doctrines among British chemists. For this purpose he not only gave Sir JAMES free access to his papers, but exhibited to him several very important experiments, even before they had been communicated to the Academy of Sciences, or made known to the chemical world in general. Sir JAMES HALL returned to Scotland in the autumn of 1787, well versed in the new doctrines, of which he became an able and zealous propagator. He had many long discussions on this subject with Dr HOPE, who was then a keen supporter of the phlogistic hypothesis, but was soon convinced by the arguments and facts communicated by his friend; and next winter he taught them to his class, the first occasion on which the Lavoisierian doctrines were introduced in a public course of lectures in Great Britain.

In the beginning of 1783 Dr HOPE was admitted as a Fellow of this Society; and soon after he resolved to pass the summer vacation in Paris.



In his way to the French capital, he made a short stay in London, where he was very kindly received by Sir JOSEPH BANKES ; and he had the high gratification of being introduced to CAVENDISH, BLAGDEN, HERSCHEL, and several other English philosophers.

At Paris he experienced marked attention from LAVOISIER and BERTHOLLET ; which he ascribed partly to his having been a pupil of Dr BLACK ; but was principally, I believe, owing to his having been the first chemist who had publicly taught the new French doctrines in Great Britain.

Dr HOPE considered this an important era in his life, as introducing him to men whose names were then becoming celebrated over Europe for their skill in a science to which he was ardently devoted. The amiable manners and great abilities of LAVOISIER made a deep and lasting impression on the Scottish professor ; and few persons more sincerely deplored the sad fate of that accomplished man, from whom he had received the most flattering attentions.

During his connection with the University of Glasgow, Dr HOPE enumerated as his colleagues and his friends, Dr THOMAS REID, the celebrated Professor of Moral Philosophy ; the eminent Mr JOHN MILLER, Professor of Law ; and Mr GEORGE JARDINE, Professor of Logic.

Dr HOPE, for some years, entertained the wish to join the practice of medicine with his chemical labours ; and in 1789, sought and obtained the appointment of assistant Professor of Medicine, and successor to his uncle Dr STEVENSON in the University of Glasgow. For two years he taught the Theory and Practice of Medicine, at the same time with Chemistry. On the death of his uncle, in 1791, Dr HOPE became the sole Professor of Practical Medicine, and then resigned the office of Lecturer on Chemistry ; but he continued his private researches in his favourite study, the first result of which was his masterly paper "*On a new mineral from Strontian.*"

This was communicated to the Royal Society of Edinburgh on the 4th Nov. 1793 ; and it proved, what indeed had been previously conjectured by others, that this mineral contained a new earth, differing decidedly in its qualities from Barytes, to which it bears the greatest affinity. To this earth Dr HOPE gave the name of *Strontites*, from the place at which it had then only been found. From the appearance of this mineral, which had been, I believe, first noticed, about six years before, by Dr WALKER, Professor of Natural History in Edinburgh, it was generally supposed to be a variety of heavy-spar, or perhaps might contain a new ingredient. Yet KIRWAN, in the Second Edition of his Mineralogy, published late in 1794, takes no notice of Strontites ; except we may consider such, his statement, "that he had heard of the discovery of *Barolite*, or aerated Barytes in Argyleshire ;" and SCHMEISSER, whose "*Mineralogy*" appeared in London two years after the reading of Dr HOPE's paper, disingenuously passing over his experiments, states, "by analysis I found it yielded 68 of Strontian earth, 30 of



carbonic acid, 1 of calcareous earth, and a little of phosphate of iron and manganese, which probably gives it colour." This would lead the unsuspecting reader to infer that SCHMEISSER had been the discoverer of the new earth, which is certainly not the case; but this is only one of the many plagiarisms of this writer. The only chemist who has the slightest claim to the merit of an original detector of Strontian earth, besides Dr HOPE, is M. KLAPROTH; who, in the *Chemische Annalen* for 1793-94, compared Strontianite with Witherite. In his first paper, KLAPROTH conjectured that the two minerals differed in composition, because the salts of Strontian colour the flame of combustibles red, while those of Barytes do not; and this conclusion was afterwards confirmed by some experiments of SULZER and BLUMENBACH. Neither KLAPROTH nor HOPE seem to have been aware of what the other had discovered, and both may therefore be considered as original discoverers, but the first full investigation of the subject is undoubtedly due to Dr HOPE.

The success of these investigations, and the popularity of Dr HOPE's Chemical Lectures at Glasgow, suggested to the celebrated Dr BLACK, then in declining health, the idea of having his promising pupil Dr HOPE associated with him, as his assistant and successor in the Chemical Chair. He accordingly made the proposal to Dr HOPE in 1795, obtained the concurrence of the Patrons, and on the 4th of November of that year, the latter body chose Dr HOPE in that capacity. In that session but a few of the lectures were delivered by Dr HOPE: But in the session of 1796-97, after Dr BLACK had concluded his admirable Lectures on Heat (as I find from M.S. notes of a friend who attended that course), the venerable Professor introduced Dr HOPE to the class in the following terms:—"After having, for between 30 and 40 years, believed and taught the chemical doctrines of STAHL, I have become a convert to the new views of chemical action; I subscribe to almost all M. LAVOISIER's doctrines; and scruple not to teach them. But they will be fully explained to you by my colleague and friend Dr HOPE, who has had the advantage of hearing them from the mouth of their ingenious author." Accordingly, Dr HOPE delivered a considerable portion of that wintercourse to a large audience; and in the summer of the year 1797, he also gave a three months' course of Chemistry.

The eminent men who were at that time the ornaments of our University, were Professors MONRO *secundus*, BLACK, GREGORY, ROBISON, DUGALD STEWART, and PLAYFAIR—and HOPE always remembered with much satisfaction his earlier intercourse with Principal ROBERTSON, ADAM SMITH, and especially with HUTTON the geologist—a constellation of names that shed a lustre on the society of Edinburgh at that period.

It would seem that the subject of our memoir still intended to conjoin the practice of medicine with his academical duties. For this purpose, he became a Fellow of the Royal College of Physicians in November 1796; and, until some



time after the beginning of this century, regularly took his share of the duties of Clinical Professor of Medicine.

Dr BLACK, who was always of a most delicate constitution, did not feel himself able to lecture after the session of 1796-97; but the life of this truly great philosopher and most accomplished teacher, was protracted to the 14th of November 1799. On his death Dr HOPE became the sole Professor of Chemistry in our University.

It was in the Session of 1798-99, that the writer of this memoir first became Dr HOPE's pupil; and he remembers, with gratitude, that it was from the clear and able prelections, and most happy experimental illustrations of the leading principles of the science by Professor HOPE, he imbibed that predilection for chemical pursuits, which long formed his chief relaxation from the severer duties of his professional life; and which, he hopes, will continue to afford interest and amusement to his declining years.

I may here remark, that Dr HOPE had become, from the variety and excellence of his illustrations, and dexterity in chemical manipulations, the most popular teacher of the science that had ever appeared in Great Britain. Not only was his lecture-room crowded with medical students from every part of the British dominions, but numerous foreigners resorted to Edinburgh, and became his pupils. Many of our nobility at that time were among his students. During one of the winters that I attended his class, among my fellow-students were the late Earl of LAUDERDALE, the present Earl (then Lord MAITLAND), Lord SEMPILL, and the late Lord ASHBURTON. The large class-room was filled to overflowing; and he who was not there before the commencement of the lecture had no chance of a seat.

The rage for chemistry continued for several years; and certainly no chemist ever had larger audiences than Dr HOPE. I find that the average number of chemical pupils here, during the six years preceding Dr HOPE's appointment as Dr BLACK's assistant and successor, was 225. When I attended him in the end of the last century and beginning of this, his annual pupils were above 400; in 1813 they had risen to 500, and in 1827 they had actually amounted to 575.

While HOPE lectured at Glasgow, the total number of his pupils amounted to about 300. After his removal to Edinburgh, his chemical lectures were attended by 15,500 persons, and the number of tickets issued for his chemical class was no less than 16,800.

His reputation as a lecturer induced a number of the Faculty of Advocates to request him to give a summer course of chemistry in 1800; which was also attended by many gentlemen engaged in other pursuits.

I shall now offer some remarks on the original investigations in which Dr HOPE at different times engaged, after his paper on Strontites.

It is well known that BOYLE, MARIOTTE, and other philosophers, ascertained



experimentally, that the diminution of bulk in atmospheric air is always proportional to the compressing force; or its volume is inversely as the pressure which it sustains; and philosophers had generally, from analogy, inferred the same of other gases.

I find, from some notes of Dr HOPE, that in 1803 he instituted a series of experiments to ascertain "whether the principal permanently elastic fluids, viz., oxygen, nitrogen, hydrogen, and carbonic acid, observe the same law of compressibility from pressure which air does."

In these experiments the compression was obtained by means of a column of mercury in a siphon tube, in the same manner as in the experiments of BOYLE, and of later experimentalists. The result was, that they all follow the same law of compression.

On the 9th of January 1804, Dr HOPE read a memoir to the Royal Society of Edinburgh, "*On the contraction of water by heat, at low temperatures,*" which appeared in the 5th volume of the *Transactions*, in 1805, p. 379.

The Florentine Academicians had published, in 1667, the singular fact, that water expands as it cools towards its freezing point; and in 1683, the same was stated to the Royal Society of London by Dr CROUNE, the Gresham lecturer. His experiments shewed that water, when cooling, begins to expand as its temperature sinks, from several degrees above the freezing point, until it begins to congeal. Several subsequent writers endeavoured to confirm these observations, but differed as to the point at which water attains its maximum density; some contending for the 40° or 41° of Fahrenheit; others for the 42° or 43°. All those experiments were made in tubes with large bulbs at one extremity, resembling in form the glass of a thermometer, but on a larger scale.

On the reading of CROUNE's paper, it was contended by Dr HOOKE, one of the most acute but most disputaceous philosophers of his age, that this expansion was apparent, not real; arising from the sudden contraction of the material of the bulb, on the application of cold. This opinion has since been maintained by several very eminent men; among whom we may mention DALTON, whose experiments on this subject are most ingenious, and who, in a private letter, drew Dr HOPE's attention to this curious phenomenon. It occurred to Dr HOPE, that this point might be decided by experiments, in which a change in the capacity of the containing vessels could have no influence on the result.

He took a cylindrical glass vessel,  $8\frac{1}{2}$  inches deep and  $4\frac{1}{2}$  inches wide, which was filled with water at the freezing point, 32°. Two delicate thermometers were suspended in the axis of the jar, so that the bulb of one was half an inch below the top of the liquid, and that of the other as far from its bottom. This apparatus was placed in a room at a temperature 60°, and the progressive temperature of the water was carefully noted, as indicated by both thermometers. The result was, that up to 38°, the lower thermometer was invariably one degree higher than the



upper; a proof that, as its temperature rose from  $32^{\circ}$  to  $38^{\circ}$ , the water had become more dense. On reversing this experiment, by placing water at  $53^{\circ}$  in a medium cooled to  $32^{\circ}$ , he found, while the temperature of the water descended to  $40^{\circ}$ , that the water at the bottom was always the coldest, and that this difference between upper and lower thermometers was sometimes as much as  $7^{\circ}$  or  $8^{\circ}$ ; but that in cooling from  $40^{\circ}$  to the freezing point, the thermometer at the bottom remained higher than that near the surface of the liquid.

The experiments of Dr HOPE, which were varied in different modes, led him to fix the point of greatest density of water at the temperature of  $39^{\circ}5$  Fahrenheit.

These well-devised though simple experiments are perfectly conclusive on the question of the greatest density of water being several degrees *above* its freezing point; and Mr DALTON, the most able advocate of the opposite doctrine, afterwards admitted the general correctness of the observation, though he considered that the greatest density was not at so high a point as Dr HOPE supposed. There are, however, many facts which would lead us to infer, that the greatest density of water cannot be far from the point assigned by HOPE—as, for instance, the remarkable uniformity of temperature in deep alpine lakes, which is about  $40^{\circ}$ , according to the observations of PICTET and others.

From a long note attached to this paper of Dr HOPE\* we also learn, that at an early period he had experimentally proved the fallacy of Count RUMFORD's assertion, that liquids were absolute non-conductors of heat. This philosopher had alleged, that when heat was applied to the upper surface of a fluid, the heat could only affect a thermometer placed *below* the surface of the liquid, by transmission downwards through the medium of the sides of the containing vessel; because, according to him, the particles of fluids communicate none of the caloric they receive to the contiguous particles (as takes place in solids), and that when heat is applied below, they become heated only by currents set in motion by the diminished gravity of the heated particles.

In these experiments, Dr HOPE employed a wide glass jar to contain the liquid to be the subject of trial, and applied heat to the surface of the liquid in a vessel 11 inches in diameter. The bulb of a delicate thermometer was placed half an inch below the surface of the liquid; and all conduction by the sides of the vessel was prevented, by keeping it immersed in water equally cold as high as the surface of the liquid within the vessel. Notwithstanding these precautions, the thermometer, in several experiments, slowly rose. The liquids subjected to such trials were water, olive-oil, and mercury.

Other experiments were conducted in a different manner. Equal portions of liquids, such as alcohol, were rapidly mixed together at different temperatures; and the mixture immediately indicated a mean temperature—which HOPE

\* *Trans. R. Soc. Edin. V.*, p. 394.



contended could not have happened, if liquids had been absolute non-conductors of caloric.

These experiments seem sufficiently conclusive; but Count RUMFORD still insisted, that the rise of the thermometer was only owing to the conduction by the sides of the containing vessel, in HOPE's experiments, as well as in the analogous investigations of THOMSON, NICHOLSON, and DALTON.

This objection suggested to the late Dr JOHN MURRAY the ingenious idea of employing a hollow cylinder of ice as the containing vessel; which, as its temperature could not rise above  $32^{\circ}$ , could not conduct or communicate any heat to the thermometer. Water could not be employed in this apparatus, on account of its anomaly in expanding by cold near its freezing point; but olive-oil, cooled to  $32^{\circ}$ , was used; and in experiments made by suspending the heating cause in contact with the surface of the oil, the thermometer rose, in a longer or shorter interval, in proportion to the greater or less depth of the instrument below the surface of the oil.—(*Nicholson's Journal*, 8vo series, I. 425.)

In considering these experiments and the objections stated, it occurred to me, that if the *same* apparatus were employed with different fluids, did the rise of the thermometer depend on the conduction of the sides of the vessel, that rise should be nearly equal, whichever liquid was employed. I tried this with ten different liquids; and though the apparatus was the same, and the distance between the source of heat and the thermometer similar, yet the time required to raise the thermometer to the same point, was very different with the different liquids: this I ascribed to the difference in the conducting power of each liquid.—(*Nicholson's Journal*, XII. 137, for 1805.)

All these investigations confirmed the view taken by HOPE, that though liquids were very slow conductors of caloric, they could not be considered, as was alleged by RUMFORD, absolute non-conductors.

Dr HOPE's reputation as a teacher of chemistry, arising from the causes already noticed, and his tact in exciting in his hearers his own enthusiasm for the study, long continued to attract vast crowds of pupils. His honours kept pace with his reputation.

In 1810 he was elected a Fellow of the Royal Society of London; in 1815 he was chosen President of the Royal College of Physicians of Edinburgh, an office which he continued to fill for four successive years; in 1820 he was admitted an honorary member of the Royal Irish Academy; and in 1823 he became one of the Vice-Presidents of this Society, an office which he held until his death. During his connection with the College of Physicians, he took an active part in the preparation of the ninth and tenth editions of their Pharmacopœia, especially in that published in 1817. For several years, besides his duties as a Professor of Chemistry, Dr HOPE gave an annual course of Clinical Medicine in this University, which was also numerously attended. But for many years before his death, he



resigned to his younger brethren the duties of the Infirmary, and of Clinical instruction.

Dr HOPE is the author of a decided improvement on the Eudiometer of SCHEELÉ, which, by permitting the convenient agitation of the included air with the liquid that absorbs the oxygen, expedites and simplifies that process; and is described in most elementary works on Chemistry.—(*See Nicholson's Journal, Vol. VI.*)

The establishment of Mechanics' Institutions, or Schools of Art for the instruction of the humbler classes, gave to that rank of society means of acquiring information beyond that usually obtained by many of the wealthier classes; and, in the opinion of some, diminished the respect of mechanics for individuals less knowing than themselves. The system of courses of popular lectures on scientific subjects for both sexes, which had prevailed for many years in various parts of England, was comparatively little practised in Scotland, when Dr HOPE delivered, in the spring of 1826, a short course of chemical lectures to Ladies and Gentlemen. His vast lecture-room was crowded with what he described to me as a "most brilliant audience;" and his example was soon followed by more than one of his colleagues in the University, and by several of the eminent men who then taught different branches of natural science in their private establishments; undoubtedly with no small benefit to the rising generation, and the more general diffusion, among all ranks, of interesting subjects of contemplation, and of conversation. Even admitting that the knowledge thus diffused is not deep, it has imparted to social intercourse, a vigour and variety that contrasts favourably with the former insipidities and frivolities of fashionable society.

Dr HOPE had always endeavoured to impress his pupils with the importance of Practical Chemistry, and introduced into the University classes for the cultivation of that branch of study; but, from increasing years, and love of ease, this department he soon almost wholly abandoned to his assistants.

In 1828, to encourage the study of chemistry among the students in the University, particularly in the practical department, he instituted a chemical prize; and, for this purpose, presented to the *Senatus Academicus* a sum of £800, as a fund, the interest of which should, annually or triennially, be given as a prize to the author of the best essay on a given chemical subject, illustrated by experiment. It should be observed, that money thus liberally bestowed, was the sum which Dr HOPE had received for his popular lectures on chemistry, which he appears from the beginning to have destined for this purpose.

For many years Dr HOPE appears to have abandoned the pursuit of original research, with which he had so auspiciously commenced his chemical career, and to have confined his efforts to the improvement of his lectures, and the devising of striking experimental illustrations.

I find no original paper of his, from the publication of his investigations on



the conducting power of fluids, until the 18th January 1836, when he read, to the Royal Society of Edinburgh, the first part of a paper entitled, "*Observations and Experiments on the coloured and colourable matters in leaves and flowers of plants, upon which acids and alkalies act in producing red, yellow, or green colours.*" A second part of this paper was laid before the Society on the 21st of the following March.

Although chemists have at all times used coloured vegetable infusions for indicating the presence of acids and alkalies, no researches appeared to have been made on the peculiar vegetable principle on which the acid and alkali acted; and it was generally taken for granted that both descriptions of agents acted on one and the same principle. Dr HOPE endeavoured to shew, by various experiments on the general colouring matter of plants, that vegetable infusions, which became red by the addition of an acid, and green or yellow by an alkali, contained two distinct principles, on one of which acids acted, and alkalies on the other. To the former he proposed the name of *Erythrogene*, and for the latter that of *Xanthogene*. DECAN-  
DOLLE had distinguished the colouring matter of flowers by the name of *Chromule*; and ELLIS speaks of the substance which may become green, red, or yellow, under different circumstances, as the *colourable matter* of plants. The object of Dr HOPE's researches was to prove, that this matter was not an individual substance, but consisted of two distinct vegetable principles, which exist either separate or combined in different plants. He illustrated this by many experiments on different sorts of plants, and gave the results in eight tables. He shewed that all green leaves, all white and yellow flowers, contain only one of these principles, viz., *Xanthogene*, that all red and blue flowers, also all leaves with red colours, contain both *Xanthogene* and *Erythrogene* (with the single exception of Litmus, which contains no *Xanthogene*), and that red flowers abound in *Erythrogene*. The distinct nature of these proximate principles of vegetables he inferred from the different modes in which they are affected by chemical re-agents.

In the same year Dr HOPE made a communication to the Society "*On the Chemical Nomenclature of Inorganic Compounds.*" He pointed out the disadvantages of the want of a discriminating and uniform nomenclature among teachers and writers on chemistry; and stated certain changes which he had for some time employed in his lectures.

The changes proposed were—

1. To discard the prefixes *proto*, *per*, *super*, *sub*, for compounds.
2. To adopt rigidly the happy suggestion of Dr THOMSON, viz., to employ the Greek numerals to denote the number of atoms or equivalents of the base of a compound, and the Latin numerals for the number of atoms of the oxygene or acid.
3. To avoid as much as possible the intermixture of Greek and Latin in numerical indications.



He added examples thus—

1 atom of base to	1	of oxygene, oxide of base.
1	...	2 ... bis oxide.
1	...	3 ... ter oxide.
2 atoms of base to	1	of oxygene, dis oxide.
3	...	1 ... tris oxide.
2	...	3 ... dis-ter oxide.

and so forth.

The general adoption of some such nomenclature, he conceived, would give a desirable accuracy to chemical language.

In a conversation with Dr HOPE in the early part of 1837, I noticed the discordant opinions held by various philosophers on the maximum density of sea-water, and asked whether he had applied to this fluid the same beautiful and simple investigations by which he had ascertained the point of greatest density in fresh water. He replied in the negative. I strongly recommended the subject to his notice; because, as it appeared to me, several geologists and hydrographers had deduced erroneous explanations of certain phenomena in the ocean from this undecided point. I added, that I should long ago have attempted to solve it, had I not considered that it would have been an interference with a subject he had already so ably discussed. He thanked me for the hint, and the consequence was, the completion of the series of experiments, which he communicated on the 2d of April 1838, to the Society, in an "*Inquiry whether sea-water has its maximum density at some degrees above its congealing point, after the manner of fresh water.*" Most philosophers seem to have assumed, that sea-water followed the same law in cooling as fresh water; and its greatest density was generally considered to be at temperature  $36\frac{1}{2}^{\circ}$  F.

Dr HOPE first tried the effect of cooling sea-water from  $40^{\circ}$  in vessels shaped like large thermometers, and found that it continued to shrink, by a diminution of temperature, like other bodies. He afterwards employed the same apparatus with which he had examined the peculiarity in fresh water; and he found, that in cooling from  $40^{\circ}$  to its freezing point, the coldest water was invariably at the bottom of the vessel. Therefore, the striking anomaly which so remarkably distinguishes the cooling of *fresh water*, does not take place in *sea-water*. The importance of this conclusion will be manifest to those who have examined the theories of oceanic currents, and the remarkable fact, that the existence of banks or shoals in the ocean is marked by a fall in the temperature of the superincumbent water.

Dr HOPE reserved the examination of the precise point of the maximum density of sea-water for a future communication—which was never made.

In 1843, the Society had two communications from Dr HOPE. The first was—"Observations on the Flowers of the *Camellia Japonica*, *Magnolia Grandiflora*, and *Chrysanthemum Leucanthemum*." This paper was read on two evenings.



the first on the 23d of January, the last on the 3d of April. The author, from the action of different re-agents on infusions of these flowers, established the existence in each of a distinct proximate principle, which, however, he had been unable to exhibit in a separate state; to these he gave the name of *Camelline*, *Magnoline*, and *Chrysanthemine*. He shewed, also, that notwithstanding the fine white of the petals of *Camellia Japonica*, they contained much iron.

The second paper, his last communication, was read on the 1st of May 1843, the very last time that Dr HOPE was ever at the meetings of our Society. It is styled "*An Attempt to explain the Phenomena of the Freezing Cavern at Orenburg.*"

This cavern is described by Sir RODERICK MURCHISON, as one of several occurring in a low hill of Gypsum. In winter, the air of this cavern feels warm to those who enter it; but in summer an intensely cold air issues from it. This has been explained by Sir JOHN HERSCHEL, as being produced by the long time the waves of heat and of cold take to penetrate to the interior of the cavern—each requiring six months to penetrate to that depth; just as SAUSSURE found, that it required, at Genève, six months for the heat of summer, or the cold of winter, to penetrate to the depth of  $29\frac{1}{2}$  feet. While admitting this general explanation, Dr HOPE considered that it would require something more to explain the forcible issue of such cold air during the summer months; and he makes an ingenious conjecture, on the part performed by the air cooled in the fissures, described as existing in the inmost recesses of the cavern, in producing that phenomenon.

The subject is very interesting though obscure; but I may observe that such streams of cold air are not peculiar to the Orenburg cave. Streams of air, cooled from  $15^{\circ}$  to  $34^{\circ}$  below the external air in the shade, are known to issue from the crevices of the small artificial hill at Rome, named *Monte Testaccio*; from the limestone grottos of *Cesi*, in the Roman states, so well described by SAUSSURE, in *Journal de Physique* for 1776; from the caves in the sandstone hill, on which is perched the miniature republic of *San Marino*; from the *Cantines* in the potstone rock near Chiavenna; from the caverns of *Caprino*, on the Lake of Lugano; and from the calcareous caves of *Hergisweil*, at the base of Mont Pilate, nearly opposite to Lucerne. What is still more extraordinary, such cold caves exist in countries the seats of not yet extinguished volcanic fire. Sir WILLIAM HAMILTON describes the cold winds issuing from the cave of *Ottajano*, at the base of Vesuvius; and in the Isle of Ischia, the air which issues from the *Ventarola* of *Funera* is as cold as  $43^{\circ}$  F., when a thermometer in the shade, without the cavern, is at  $58^{\circ}$ —(See Saussure, *Voyages dans les Alpes*, III. 1405.)

Such are the chief contributions of Dr HOPE to physical science.

It has been alleged that they are fewer and less important than we had reason to expect, from the long period during which he filled the Chemical Chair,



his acknowledged skill in experiment, and the brilliant path then opening for important discoveries in chemistry, which have immortalized the contemporary names of BLACK, PRIESTLEY, DAVY, WOLLASTON, DALTON, and FARADAY among ourselves—of LAVOISIER, BERTHOLLET, VAUQUELIN, GAY LUSSAC, VOLTA, KLAPROTH, BERZELIUS, and LIEBIG on the Continent. That there is foundation for this criticism, I will not attempt to deny : and, indeed, Dr HOPE seems to have anticipated it, by some observations he once made verbally to myself, and has stated in a paper now in my possession, as his apology. “Those,” says he, “who devote themselves to the science of chemistry, may be divided into two classes—1<sup>st</sup>, Those whose labours are employed in original researches, to extend our knowledge of the facts and principles of the science. 2<sup>dly</sup>, Of those whose business it is, from university or other appointments, to collect the knowledge of all that has been discovered, or is going forward in the science, to digest and arrange that knowledge into lectures, to contrive appropriate and illustrative experiments, and devise suitable apparatus for the purpose of communicating a knowledge of chemistry to the rising generation, or others who may desire to obtain it. From my professional situation, I consider myself, as Dr BLACK had done before me, as belonging to the second class of chemists. I consider my vocation to be the teaching the science.”

It is true that it is the paramount duty of one appointed to teach a science to make that his principal object ; but this, I humbly conceive, is quite consistent with most extensive original research. It may be that the regular recurrence of the labour of teaching the elements of a science, requiring several hours of daily personal exertion, may sometimes indispose a lecturer to experimental investigations of a similar kind ; but such has not been its effects on DAVY, THOMSON, BERZELIUS, or LIEBIG ; all of whom have combined the business of teachers of chemistry with the most valuable and laborious original researches. Dr BLACK had certainly made all his great discoveries before he was Professor in the University of Edinburgh ; but his health was always very delicate, and his example can scarcely be pleaded for one who enjoyed such uninterrupted and vigorous health, that he never was a single day prevented from lecturing by indisposition, for a period of more than fifty years.

Dr HOPE undoubtedly fulfilled admirably the duty of a public teacher of chemistry, as we have already stated. His mode of lecturing was methodical and clear, though his style was occasionally too laboured ; he scarcely ever failed in the performance of the nicest and most difficult experiments, which he introduced to an extent previously never attempted in chemical prelections ; and he possessed the faculty of impressing his hearers with just notions of the importance and interest of the science. Still it is to be regretted, that one so well qualified to advance the boundaries of the study, had limited his ambition and his exertions



almost so exclusively to the business of methodizing and detailing the discoveries of others.

We may here remark, that besides the eminent philosophers already mentioned as his friends, HOPE was on terms of very friendly intercourse with WATT, DALTON, WOLLASTON, and DAVY. His acquaintance with the latter began in 1799, ere that illustrious man had yet risen to celebrity. In passing through Bristol, HOPE visited the Pneumatic Institution of Dr BEDDOES, and was much struck with the originality and inventive genius of young DAVY. Soon afterwards, a lecturer of talent was wanted to fill the Chemical Chair in the Royal Institution established in London, under the management of Count RUMFORD. Dr HOPE was consulted; he strongly recommended DAVY to the notice of the Count; and in 1801, the young chemist was established in the Royal Institution. This anecdote, which I have extracted from the original correspondence, once in my hands, is honourable to the discernment of HOPE, who thus early recognised that energetic genius, which was destined to win the proudest laurels in the career of physical discovery.

Among Dr HOPE's most intimate friends in Scotland, were Dr HUTTON, the geologist, and Sir JAMES HALL. From the intercourse with these eminent men, he had early imbibed their geological tenets; and for many years he was the only public teacher of science in this country, who inculcated the doctrines of the *Plutonic* theory of the earth. During the many years of my studies in this University, HOPE regularly gave several interesting lectures on geology in his chemical course, and was a strenuous assertor of the truth of the Huttonian theory, which he continued annually to teach in many subsequent years; while the rival Wernerian doctrines were most ably, and no less strenuously maintained, by my friends, Professor JAMESON, and the late most eminent and eloquent lecturer Dr JOHN MURRAY. At that time the chemical history of mineral bodies formed no inconsiderable part of a course of chemistry; and it was in introducing the mineral kingdom to the notice of his pupils, that Dr HOPE exhibited many of the proofs of the igneous formation of stony bodies; which was also illustrated by a well-selected series of rocks, chiefly collected by himself in different excursions in the Highlands and Western Isles, and in various other parts of the United Kingdom.

For many years Dr HOPE enjoyed uncommon health, and continued to discharge the duties of the Chemical Chair with his usual success, until within a year of his death.

A few years before that event, he complained to me of inability to read by candlelight, and of suffering severe pain in his eyes on making the attempt. On examining his eyes, I discovered on each cornea those minute depressions like the marks of the point of a pin, which have been described by some authors as abrasion.



or commencing ulceration of the cornea. The daily use of a weak solution of nitrate of silver gradually removed the disease; but, after some months, it recurred in a less violent degree, and again yielded to the same remedy.

In 1838, on completing the fiftieth year of his career as a Professor of Chemistry, Dr HOPE was invited to a public dinner by a numerous body of his former pupils. The meeting was attended by many philosophers from a distance, as well as by a great number of the inhabitants of Edinburgh. It was on this gratifying occasion that he stated, among other causes of thankfulness, that he never had been for a single day, either as a student or as a teacher, detained from the duties of his class.

Dr HOPE had continued his lectures in the University until the conclusion of the winter session in 1843. It was observed, that his voice was feeble, and although his experiments were, as usual, neatly performed and successful, that he had lost something of his wonted energy. Increasing debility induced him, in the autumn of that year, however, to resign his Professorship, rather unexpectedly, a short time before the commencement of the session of 1843-44; so that the Patrons had not sufficient time to deliberate on the choice of a successor in this important Chair. In the mean time, it was very necessary for the interest of the University, that a course of chemistry should be there delivered as usual. I was then in England; but, at the earnest request of the Senatus Academicus and the Patrons, after some hesitation, I undertook the duty, and taught the chemical class during the session of 1843-44. I know that Dr HOPE also was gratified by my undertaking the task. He not only freely gave me the use of his manuscript lectures, which were fairly and fully written out, and of his whole apparatus, but relinquished, in my favour, that portion of the emoluments of the class which had been secured to him as an annual retiring allowance, by the terms of his resignation.

It is but justice to Dr HOPE to state, that I found his lectures far more nearly written up to the advanced state of chemistry at that period, than I had been led to expect; and although it was necessary to make various alterations and additions, especially in the disquisitions on organic chemistry, these alterations and additions were less extensive than I had anticipated. Whether he had employed the interval between his last course and mine in improving his manuscript, I cannot tell; but the fact I have mentioned ought to be recorded. During that winter I had much intercourse with Dr HOPE. He was pleased to express a strong interest in my exertions, and said, that he had frequently enquired from others how I carried on the duties of the chemical class.

In the end of 1843 and beginning of 1844, he seemed rather more vigorous than in the preceding autumn; but as the spring advanced, his strength began very visibly to fail, and he spoke of his gradual decay with firmness and resignation.



During the month of May, he was much in bed ; yet even then he took an interest in general conversation, and warmly congratulated me on the termination of my chemical labours.

A few days before his death I saw him for the last time, and although apparently not in suffering, he took leave of me as if we should meet no more.

He quietly expired on the 13th of June 1844, in the 78th year of his age.

Dr HOPE was never married. An excellent portrait of him, by the late Sir HENRY RAEBURN, which has been engraved, is in the possession of his family; and a fine bust of him by our eminent artist STEELL was presented to the University.



XXIX.—*On the Colouring Matter of the Morinda citrifolia.* By THOMAS ANDERSON, Esq., M.D.

(Read 17th April 1848.)

The chemistry of the colouring matters has, perhaps, scarcely as yet met with the extended and complete investigation which the importance of the subject, in a theoretical and practical point of view, appears to deserve. The attention of chemists has been almost exclusively directed to the study of a comparatively small number of these substances, such as indigo, logwood, and the colouring matters of the lichens, which have been well and completely investigated; while the remaining, and by far the more extensive class, has received only a very partial and imperfect examination. To the latter, however, belong some of the most important of our dyes; and among others, the most valuable and indispensable of all, madder namely, the chemistry of which forms a problem as yet very far from being solved, but which chemists have shewn little disposition to submit to a thorough and searching investigation; and this disinclination seems to continue, notwithstanding that ground has been broken on the subject by the important observations of ROBIQUET, KUHLMANN, RUNGE, and others, which, though extremely incomplete, serve at least to indicate the importance of the results it is likely to afford, and to clear away the preliminary difficulties by which the commencement of such an investigation is surrounded.

But madder is only one member of an extensive class of dye-stuffs, each of which contains one or more colouring matters, the chemical constitution and relations of which are almost entirely unknown; and it may seem surprising that, with the important results obtained from those already examined before them, chemists should not have attempted to work out more completely than has yet been done, the rich mine of facts which they present, and the full exploration of which is equally important to theoretical chemistry and to its practical applications. The reason, however, in all probability is, that they have been deterred from the investigation by the small quantity of actual colouring matters which most of these substances contain, and the tedious and complicated processes requisite for their preparation. In indigo, and those which have been fully investigated, the colouring matters are supplied to us in the arts in any quantity, and in a state approaching, at least, to purity; but in roots and plants, the case is very different, as they there constitute only a minute fraction of the whole mass, from which their separation is always attended by difficulties, and necessitates



operations on a larger scale than is either convenient or customary in a chemical laboratory.

I have experienced this difficulty to a considerable extent in the investigation of the colouring matter to be treated of in the following communication, which has been somewhat restricted by the limited quantity of the substance at my disposal. I do not, therefore, present it to the Society as completely exhausting the subject, which I still leave open for further researches, but principally because the colouring matter in question differs in certain remarkable points from any hitherto described, and constitutes the type of an entirely new class, the existence of which is likely to throw light on some obscure points of Technical Chemistry.

The subject of these experiments was imported into Glasgow, some time since, under the name of Sooranjee, with the intention of introducing it as a substitute for madder in the art of dyeing. For this purpose it was, on its arrival, submitted for trial to some of the most experienced and skilful calico-printers in Glasgow, all of whom concurred in declaring it not to be a dye at all, and to be totally destitute of useful applications. My friend Professor BALFOUR happening to hear of this circumstance, was so good as to obtain for me a quantity of the root, which has enabled me to submit it to a chemical investigation. At the time I received the substance, no information could be got with regard to the plant from which it was obtained; but at the request of Dr BALFOUR, the importers took the trouble of writing to their correspondents in Bombay, for the purpose of obtaining specimens of the plant or its seeds. The result of this application was, that we soon received a small packet of seeds, the label of which bore that they were those of the sooranjee or soorinjee plant, the *Morinda citrifolia* of botanists. As this plant has been long and familiarly known as yielding one of the most extensively employed native Indian dyes, and as no authority was given with the seeds for the determination of the species, it was considered desirable to substantiate it by growing them, and examining the plant itself. They were accordingly sown, both in the Botanic Garden, and in the garden of Professor SYME at Milbank; unfortunately, however, not a single seed germinated, and we were compelled to content ourselves with the less satisfactory process of determining the plant by the characters of the seed itself. By a comparison with the plates of GÆRTNER'S\* work, they are found to agree very closely with his figures of the seeds of the *Morinda citrifolia*, and certainly belong to a species of the genus. Of this genus six or seven species are known to produce dyes,† but of these two only are important, the *M. citrifolia* of LINNÆUS, and the *M. tinctoria* of ROXBURGH, both of which are extensively cultivated in various parts of India, for the sake of

\* De Fructibus et Seminibus Plantarum, vol. i., p. 144.

† In addition to those above mentioned, colouring matters are contained in *Morinda multifida*, *angustifolia*, *chachuca*, and *umbellata*.



the dye they contain. According to Dr BALFOUR, however, some confusion exists with regard to these two species, which differ so slightly, that it is doubtful whether they ought not to be conjoined, the sole difference consisting in the leaves, which are shining in the *citrifolia*, and not shining in the *tinctoria*, in the former oval, in the latter oblong. All things taken into consideration, Dr BALFOUR is of opinion that we are perfectly safe in referring the sooranjee to the *Morinda citrifolia*, which has been long described as the source of the native dye.

The *Morinda citrifolia* has been described by RHEEDE\* under the name of *Cada pilava*, and is referred by botanists to the *Bancudus latifolia* of RUMPHIUS,† though it is curious that he expressly states that the roots of this species possess no dyeing properties, while he is very explicit regarding those of his *Bancudus angustifolia*, the *M. umbellata* of modern botanists, and the Wongkudu of the Javanese dyers, by whom it is employed to produce a beautiful scarlet. A detailed account of the cultivation of the *M. citrifolia*, and its employment as a dye, is given by Mr HUNTER,‡ who states that it is known by the name of Aal in Malawa, and of Atchy in Oude. No experiments, so far as I know, have been made on the chemistry of its colouring matter, unless we except some observations of Dr BANCROFT,§ on a root sent from India under the name of Aurtch, resembling madder in its external appearance, and which, from the analogy of the native names, he conjectures to be the *M. citrifolia*; no definite proof, however, is given, as Dr BANCROFT had not seen the plant, and I am inclined to doubt their identity, as the characters he ascribes to it do not agree with those of the substance I have examined. With regard to the term Sooranjee, I have been able to obtain no information in any of the works on the natural productions of India, nor is any one of whom I have had an opportunity of inquiring acquainted with the name.

Sooranjee is the root of the plant, and is imported cut up into pieces from one to four inches in length, and varying in diameter from half down to nearly an eighth of an inch. On the small pieces the bark is thick, and forms a large proportion of the whole root, but on the larger fragments it is much thinner. Its external colour is pale greyish-brown; but when broken across, it presents colours varying from fine yellow into brownish-red, and confined principally to the bark. The wood itself has only a slight yellowish shade, deepest in the centre, and scarcely apparent close to the bark;|| but it is coloured dark red by alkalies, in-

\* RHEEDE, Hortus Malabaricus, vol. i., p. 97.

† RUMPHIUS, Herbarium Amboinense, lib. v., cap. 13.

‡ Asiatic Researches, vol. iv., p. 35.

§ Philosophy of Permanent Colours, vol. ii., p. 308.

|| This is also mentioned by RUMPHIUS as a character of the woody part of the roots and stem of his *Bancudus angustifolia*.



dicating the presence of a certain quantity of colouring matter in it. The bark is readily detached, and its inner surface, as well as that of the wood, has a peculiar silvery appearance, most apparent on the large pieces, and almost entirely absent in the smaller. Boiled with water, it gives a wine-yellow decoction, and with alcohol a deep red tincture.

*Morindine.*

For the preparation of the colouring matter of sooranjee, to which I give the name of Morindine, I at first attempted the use of boiling water, in which my preliminary experiments had shewn it to be pretty soluble; I found, however, that this method was inapplicable, as the decoction contains a quantity of mucilaginous matter which hinders the filtration of the fluid. The use of alkalies, in which the colouring matter is rapidly dissolved, likewise proved abortive, and I had finally recourse to alcohol, which succeeded perfectly. The bark of the root, separated from the woody portions and ground to fine powder, was boiled with six times its weight of rectified spirit, and the tincture filtered boiling hot. Its colour was deep brownish-red, and, on cooling, it let fall the greater quantity of the colouring matter as a brown flocculent precipitate, containing the morindine, contaminated by another red colouring matter which exists in the root in small quantity only. A second decoction, with an equal quantity of spirit, gave a paler solution, from which morindine was deposited with a much smaller quantity of the red colouring matter. This treatment was repeated over and over again, as long as the tincture deposited anything on cooling, and every successive boiling produced it purer than the preceding, until at length, from the final decoctions, it made its appearance in the form of minute radiated crystals of a yellow colour. By successive crystallizations from alcohol of 50 per cent., the red matter with which it was mixed was entirely removed, and the morindine obtained of a fine yellow colour. It was still, however, impure, and contained a quantity of ash, amounting, in one experiment, to 0.47, in another to 0.32 per cent. The separation of this could not be effected by crystallizations from alcohol alone; but after some trouble I succeeded in removing it completely by solution in alcohol slightly acidulated by hydrochloric acid, from which it crystallized in a state of purity.

Morindine is deposited from alcohol in minute needles, which, if the solution be dilute, make their appearance in radiated circles attached to the glass, and resembling, in their arrangement, the crystals of wavellite. They are extremely soft, and, on being detached, collected on a filter, and dried, mat together into a mass, presenting a rich sulphur-yellow colour, and satiny lustre. These crystals are sparingly soluble in cold alcohol, much more so in boiling spirit, especially if dilute; and the fluid on cooling is filled with a mass of bulky needles, which, when dried, shrink into a very small bulk. They are much less soluble in absolute al-



cohol, and totally insoluble in ether. Water dissolves morindine in the cold very slightly, although sufficiently to communicate a yellow colour to the fluid; at the boiling temperature, however, it is readily taken up, and again deposited, on cooling, as a gelatinous mass, destitute of all traces of crystallization, which stops up the pores of the filter, and prevents the separation of the mother liquor. It dissolves in solutions of the alkalis, with a fine orange-red colour. With concentrated sulphuric acid it gives a deep purple, which is violet in thin layers. After twenty-four hours' contact, the solution, on being diluted, deposited yellow flocks of the colouring matter in an altered condition, as it was now totally insoluble in cold water, and gave, with ammonia, a violet and not an orange solution. Nitric acid, sp. gr. 1.38, dissolves morindine slowly in the cold, with a deep brownish-red colour. The application of heat immediately produces violent action, the brown colour disappears, and nitrous acid fumes are evolved. The fluid, after long-continued boiling with the acid, and neutralisation with ammonia, gave no precipitate with salts of lime.

Solution of morindine gives, with subacetate of lead, a precipitate depositing itself in crimson flocks, which is extremely unstable, and cannot be washed without losing colouring matter. With solutions of baryta, strontia, and lime, it gives bulky red precipitates, sparingly soluble in water. Perchloride of iron produces a dark brown colour, but no precipitate. When its ammoniacal solution is added to that of alum, the alumina precipitated carries down with it the morindine as a reddish lake, and, when added to perchloride of iron, a brown precipitate is thrown down, which cannot be distinguished from pure peroxide of iron, but which contains morindine, as the supernatant fluid is colourless.

Heated in close vessels, morindine melts into a deep brown fluid, and boils at a high temperature, with the evolution of an exceedingly beautiful orange vapour resembling that of nitrous acid, which deposits itself on cold substances in fine red needles of considerable length. A bulky charcoal remains in the vessel.

The analyses of morindine were performed with oxide of copper, and upon substance which had been carefully dried for a long time at 212°. The results were as follows:

$$\text{I. } \left\{ \begin{array}{lll} 6.406 \text{ grains of morindine gave} \\ 13.028 & \dots & \text{carbonic acid, and} \\ 2.990 & \dots & \text{water.} \end{array} \right.$$

$$\text{II. } \left\{ \begin{array}{lll} 5.956 \text{ grains of morindine gave} \\ 12.100 & \dots & \text{carbonic acid, and} \\ 2.699 & \dots & \text{water.} \end{array} \right.$$

$$\text{III. } \left\{ \begin{array}{lll} 4.564 \text{ grains of morindine gave} \\ 9.270 & \dots & \text{carbonic acid.} \end{array} \right.$$



	I.	II.	III.
Carbon, . . .	55.46	55.40	55.39
Hydrogen, . . .	5.19	5.03	...
Oxygen, . . .	39.35	39.57	...
	<hr/> 100.00	<hr/> 100.00	

These analyses give the formula  $C_{28}H_{15}O_{15}$ , which agrees perfectly with the mean of the experimental results, as is shewn by the following calculation.

	Calculation.	Mean of Experiment.
28 Equivalents Carbon, . . .	2100.0      55.44	55.41
15    ...    Hydrogen, . . .	187.5      4.95	5.11
15    ...    Oxygen, . . .	1500.0      39.61	39.48
	<hr/> 3787.5      100.00	<hr/> 100.00

The formula thus ascertained brings out an interesting relation between morindine and the colouring matters of madder, and more especially that one which is obtained by the sublimation of madder purple. From his analysis of this substance, SCHIEL\* deduces the formula  $C_7H_4O_4$ . As this, however, is no more than the simplest expression of the analytical results, and as all the other madder colouring matters examined contain 28 equivalents of carbon, we are justified in supposing its real constitution to be represented by quadruple of that formula, or  $C_{28}H_{16}O_{16}$ , which differs from that of morindine by a single equivalent of water only. The unsublimed madder purple is also connected, though more remotely, with morindine, and differs only by containing 5 equivalents of hydrogen less, its formula, according to SCHIEL, being  $C_{28}H_{10}O_{15}$ .

Moreover, this similarity is not confined to their formulæ only, but extends itself over all their physical and chemical properties, which approximate very closely, although they are sufficiently distinct to preclude the possibility of their being confounded with one another. And this is a point well worthy of observation, as illustrating the similarity in chemical constitution of plants so nearly related in the botanical system; the morinda belonging to the natural family Cinchonaceæ, which, by many botanists, is considered as merely a section of the Rubiaceæ, of which madder is the type.

This similarity, however, does not extend itself to their properties as dyes, in which respect they differ in a very remarkable manner. I have already mentioned that the calico-printers had entirely failed in producing a colour by means of sooranjee; and this I have fully confirmed as regards the common mordants. I digested morindine for a long time, in a gradually increasing heat, with small pieces of cloth mordanted with alumina and iron, but nothing attached itself, and

\* Annalen der Chemie und Pharmacie, vol. lx., p. 74.



the mordants, after boiling for a minute or two with soap, were found to be unchanged. Even with the root itself, alum mordant only acquired a slight reddish-grey shade, and iron became scarcely appreciably darker in colour. The case was different, however, when cloth mordanted for Turkey-red was employed. I obtained from Glasgow pieces of calico prepared for Turkey-red both by the old and new processes, and I found that both acquired, with morindine, in the course of a couple of hours, or even less, a dark brownish-red colour, devoid of beauty, but perfectly fixed. These observations agree with the account given by Mr HUNTER of the method of dyeing with the *M. citrifolia* employed by the Hindoos. The cloth is first soaked in an imperfect soap made by mixing the oil of the *Sesamum orientale* with soda ley. After rinsing and drying, it is treated with an infusion of myrobalans (the astringent fruit of the *Terminalia chebula*), and exposed for four or five days in the sun. It is then steeped in solution of alum, squeezed, and again exposed for four or five days. On the other hand, the powdered roots of the morinda are well rubbed with oil of sesamum, and mixed with the flowers of the *Lythrum fruticosum* (ROXBURGH), or a corresponding quantity of *purvius* (the nut-gall of a species of mimosa). The whole is introduced along with the cotton into a large quantity of water, and kept over a gentle fire for three hours, when the temperature is brought to the boiling point. The red colour so obtained is, according to Mr HUNTER, more prized for its durability than its beauty. This is simply a rude process of Turkey-red dyeing. He also mentions that, by means of iron mordant, a lasting purple or chocolate is obtained, but in this case the colour is probably affected by the tannin of the astringent matters employed in the process.

#### *Morindone.*

It has been already mentioned that morindine, when heated, is entirely altered, a quantity of carbonaceous matter being left, and a crystallizable principle sublimed, differing in its properties from the original substance. To it I give the name of Morindone.

Morindone is obtained by sublimation in the form of long needles, which, under the microscope, are found to be four-sided prisms, terminated by a single oblique face, and of an exceedingly rich and beautiful red colour. They are totally insoluble in water both hot and cold, but dissolve readily in alcohol and ether, and the solutions by slow evaporation deposit crystals. The alkalis dissolve it with a magnificent violet colour. In strong sulphuric acid it is also soluble, with the same intense violet colour, and it is precipitated on diluting the acid. Its ammoniacal solution gives a fine red lake when added to solution of alum, and a cobalt-blue precipitate with baryta water. The quantity of morindone which I was able to obtain for analysis was too small to admit of accurate results, or of all the precautions for its purification which would have been



resorted to had I possessed a larger quantity. The sublimed crystals were simply washed with ether, in order to remove empyreumatic matters, and then dried at  $212^{\circ}$ . Analysis gave the following results:

1.629	grains of morindone gave
3.931	... carbonic acid, and
0.614	... water,

which approximates most nearly to the formula  $C_{28}H_{10}O_{10}$ , as is shewn by the following comparison.

Experiment.		Calculation.		
Carbon,	65.81	65.11	$C_{28}$	2100.0
Hydrogen,	4.18	3.87	$H_{10}$	125.0
Oxygen,	30.01	31.02	$O_{10}$	1000.0
	100.00	100.00		3225.0

Of course, it is impossible to consider a formula as established by a single analysis upon so small a quantity. I think it probable, however, that that given above may be the true one, and that the excess of carbon was due to imperfect separation of empyreumatic matters, as, to avoid loss by solution, I washed with the smallest possible quantity of ether. That morindone is formed from morindine by the elimination of water, derives confirmation from the change which the latter substance undergoes in contact with sulphuric acid. As already mentioned, it then becomes insoluble in water, and gives a violet colour with alkalis similar to that produced by morindone, and as sulphuric acid in general acts by removing water, the probability is, that it has deprived the morindine of 5 equivalents, and converted it into morindone; at the same time this is a point which can only be determined by analysis, and the quantity which I obtained was not nearly sufficient for that purpose. Should further experiments establish  $C_{28}H_{10}O_{10}$  as the true formula of morindone, we have another simple relation with the madder colouring matters, as it would differ from madder red by a single equivalent of water, the formula for that substance, according to the analysis of SCHIEL, being  $C_{28}H_9O_9$ . It would also be polymeric with gentianin, for which BAUMERT\* has established the formula  $C_{14}H_5O_5$ .

Morindone is a true colouring matter, and is capable of attaching itself to common mordants. It gives with alumina a deep rose red, and with iron violet and black; but the colours are not very stable, and it has a strong tendency to attach itself to the unmordanted parts of the cloth, and to degrade the white. Morindine, after treatment with sulphuric acid, is capable of attaching itself to ordinary mordants.

The discovery of a peculiar colouring matter capable of fixing itself exclu-

\* *Annalen der Chemie und Pharmacie*, vol. lxii., p. 106.



sively on Turkey-red mordant, is of interest, as establishing the existence of a peculiar class of dyes hitherto totally unsuspected,—a class which may be extensive, and may yield important substances. It may serve also, in some respects, to clear up the *rationale* of the process of Turkey-red dyeing, which has long been a sort of opprobrium of chemistry. Although that process has been practised for a century in Europe, and has undergone a variety of improvements, no clear explanation of it was for a long time given, but it was supposed that, by the action of the dung, of which large quantities are employed, the cloth underwent a species of *animalisation*, as it was called, by which it acquired the property of receiving a finer and more brilliant colour than could be attached to it by purely mineral mordants. Recent experiments have, however, shewn that the oil, which is largely employed in the process, undergoes decomposition by long exposure to the air in contact with decomposing animal matter, and is converted into a sort of resinous matter, which constitutes the real mordant for Turkey-red. This has been pretty clearly made out by the experiments of WEISSGERBER.\* He found that when cloth had been treated with oil, so as to give, when dyed, a fine rose-red colour, he could, by digestion with acetone, extract from it the altered oil; and as it was removed, the cloth gradually lost the power of attracting the colouring matter of madder, until, when it was entirely separated, the cloth passed through the dye without acquiring any colour. On the other hand, he found that, by applying the substance extracted by acetone in sufficient quantity to cloth, he could obtain the richest and deepest colours with madder, without the addition of any other substance whatsoever. These observations receive additional confirmation from the experiments detailed in the present paper, as it must be sufficiently obvious that the dark red colour obtained on Turkey-red mordant with morindine, must be entirely irrespective of the alumina, on which that substance is incapable of fixing.

I fully agree with the opinion expressed by PERSOZ that the use of alum mordant, which is at present always employed in Turkey-red dyeing, will be entirely abandoned so soon as calico-printers have learned the method of modifying it with the oil which they employ, so as to bring it at once into the state in which it acts as a mordant. Some steps have been made in this direction, by making use of some chemical agents, as nitric acid and chloride of lime, for the purpose of acting on the oil; but the improvements which have been effected stop far short of what I believe will eventually be effected, when the system of pure empiricism which has been all along employed in this particular process of dyeing is abandoned, and the subject submitted to really scientific investigation. It is understood that M. CHEVREUL has entered upon the inquiry, and in his hands there is little doubt but that it will meet with a satisfactory solution.

\* PERSOZ, Sur l'Impression des Tissus, vol. iii., p. 176.







XXX.—*Notice of the Orbit of the Binary Star  $\alpha$  Centauri, as recently determined by Captain W. S. JACOB, Bombay Engineers. By Professor C. PIAZZI SMYTH, F.R.S.E.*

(Read, April 5, 1848.)

The object of this short notice is merely to submit to the Society some astronomical results which were recently communicated to me in a letter from my friend Captain JACOB, as they appeared not only to be of a highly interesting nature in themselves, but imperatively to require being followed up farther, and as the observer has lately been obliged by bad health to resign his situation in India, it seemed advisable, for the purpose of procuring attention to the subject elsewhere, to make its peculiarly interesting features as generally known as possible amongst scientific men; and as  $\alpha$  Centauri is already in a manner identified with Scotland, through the researches of the late Professor HENDERSON, and his determination of the parallax, no medium can be more appropriate than the Transactions of the Royal Society of Edinburgh.

The star  $\alpha$  Centauri, situated in  $14^{\text{h}} 29^{\text{m}}$  A.R., and  $150^{\circ} 12'$  N.P.D., is in many respects a notable object, and though its greatest claims to attention have all arisen within the last few years, under the applications of the advanced astronomy of the present day, yet even to the naked eye it has much to raise it above the general crowd. It is a star of the first magnitude, and one of the brightest indeed of that class, and is situated in a peculiarly splendid region of the sky, the same as that occupied by the Southern Cross; a constellation, by the way, which, on account of its small dimensions, and the few stars it contains visible to the naked eye, is by no means entitled to the too warm encomiums so lavishly bestowed upon it so generally by the early Southern navigators and travellers. (And here I may be perhaps allowed to point out an error in PURDY'S Hydrography, where, amongst other fine qualities attributed to the Cross, he adds that of its forming always a sort of clock to the inhabitants of the Southern hemisphere; for the longer diameter of the Cross standing vertical, as he says, at midnight, persons may always judge by the inclination of the Cross to the one side or the other, when the middle of the night may have passed. Now the two stars at either end of the longer diameter having the same right ascension, will certainly stand in a vertical line when on the meridian, but will of course only be on the meridian above the pole at midnight, once in the course of the year.) The region of the Cross, however, abundantly compensates for the poverty of the constellation itself, for such is the general blaze of star-light from that part of the sky, that a person is immediately made aware of its having risen above the hori-



zon, though he should not be at the time looking at the heavens, by the increase of general illumination of the atmosphere, resembling the effect of the young moon.

This excessive splendour is caused not only by the profusion of first, second, and third magnitude stars in the neighbourhood, but by the extraordinary general breadth and brightness of the Milky Way thereabouts; for, separating into so many distinct luminous clouds, as it were, and exhibiting between them void black spaces unchequered by a single luminous object of any kind whatever, it forcibly impresses the idea of our being situated there near the confines of the sidereal system, or in the southern side of the vast ring in which the generality of the stars are arranged. The superior brightness of so large a proportion of the stars is then naturally accounted for by their greater proximity to us; and this fact was actually *proved* by my predecessor, who found from his own observations of  $\alpha$  Centauri, an annual parallax of the large amount of 1", *i.e.*, that at the distance of this star, the radius of the earth's orbit, or 95 million of miles, subtended an angle of 1"; the greatest quantity previously found for any star in the Northern hemisphere being only 0.23".

Professor HENDERSON's results were fully confirmed by a very much longer series of observations subsequently made at the Cape Observatory by different observers, and with different instruments, and he then computed his old observations of the other principal stars in that region, and finding a considerable number\* which shewed also indications of a sensible parallax, he immediately sent out a notice of the results to the present energetic Director of the Cape Observatory, for the purpose of procuring from him a greater number of observations of those suspicious stars. Such a series was accordingly commenced, and is still going on, and we may expect before long to hear of trustworthy results having been obtained, and there is little doubt that these labours will still more strongly tend to establish the proximity of that part of the sky.

On the application of the telescope to  $\alpha$  Centauri, it proves to be composed of two stars, one very much brighter than the other, but still both may be placed in the list of first magnitude, the smaller occupying the lowest possible step in that grade. Early observers have indeed assigned it a much smaller rank, and in the British Association Catalogue published only two years ago, and intending to apply to the year 1850, it is actually made as low as the fourth magnitude; this, however, is manifestly an error, for the present epoch, as I can state from the experience derived from making the observations which served to confirm Pro-

* $\beta$ Hydri.	$\eta$ Argus.	$\epsilon$ Centauri.
$\alpha$ Phœnicis.	$\alpha$ Crucis.	$\alpha$ Trianguli Austr.
$\alpha$ Eridani.	$\gamma$ Crucis.	$\beta$ Trianguli Austr.
$\alpha$ Columbæ.	$\beta$ Crucis.	$\alpha$ Pavonis.
$\epsilon$ Argus.	$\beta$ Centauri.	$\alpha$ Gruis.



fessor HENDERSON's parallax; for, during the whole year, there was not a single day when, if the larger star was seen at all, the smaller one was not abundantly visible also; and during that part of the year when they transited the meridian by daylight, they were even then invariably seen with the mural circle telescope, whatever the state of the atmosphere, unless actual clouds intervened. But that the smaller star was never in ages past as low as the fourth magnitude, the marvellous change which has occurred in the case of  $\gamma$  Argus in our own times, would render a most hazardous assertion.

A proper motion of the large amount of  $3.58''$  is participated in by both the stars, a fact which pretty clearly proves a physical connection between them; for while they are now very nearly in the position they were in 100 years ago, when observed by the Abbé LACAILLE, they would have separated by this time upwards of five minutes, if one only was pursuing this anomalous path amongst the rest of the stars.

The first person to remark on this physical connection was Professor HENDERSON, who, in the concluding paragraph of his memoir on the parallax, says,

"The two stars appear to be approaching each other. The earliest observations of  $\alpha$  Centauri made with a telescope which I have found, are those of RICHER at Cayenne in 1673, but neither he nor HALLEY, who observed it at St Helena in 1677, mentions it as being double. Their telescopes were of course anachromatic, and probably not of much power. FEULLÉE appears to have been the first person who observed the star to be double, as he mentions in the journal of his voyage in South America in July 1709. LA CONDAMINE next observed the star during the scientific expedition to Peru for measuring an arc of the meridian." But neither of them made any observations of real service in determining the nature of the physical connection of the two stars. "From LACAILLE's observations in 1751-2, the distance of the two stars appears to have been then  $22.5''$ . MASKELYNE, who observed them at St Helena in 1761, says (*Philosophical Transactions*, 1764, p. 383), The bright star in the foot of the Centaur, marked  $\alpha$  in the catalogues, when viewed through a telescope, becomes divided into two stars, one of which is about the second and the other the fourth magnitude. They were both observed by the Abbé DE LACAILLE. I found their distance by the divided object-glass micrometer, fitted to the reflecting telescope, to be  $15''$  or  $16''$ . I have not found any observations," continues Professor HENDERSON, "of the distance of the two stars made between 1761, and the institution of the Paramatta Observatory: there, in the end of 1825 or the beginning of 1826, the distance was observed to be  $23''$ " (*Memoirs of Astronomical Society*, Vol. iii., p. 265), since which time it has been decreasing at the rate of more than half a second *per annum*. The angle of position scarcely appears to have changed since LACAILLE's time, whence it may be inferred, that the relative orbit is seen projected into a straight line or very excentric ellipse; that an apparent maximum of distance was attained in the end of



the last or the beginning of the present century; and that about twenty years hence the stars will probably be seen very near each other, or in apparent contact, but the data are at present insufficient to give even an approximation to the major axis of the orbit and time of revolution."

The next authority on the subject is Sir JOHN HERSCHEL, who specially applied himself to the subject of the Southern double stars when at the Cape, and had far superior instruments for such a purpose to any of his predecessors; he thus describes and sums up all that was known to him of this star, in his recently published work.

"This superb double star, beyond all comparison the most striking object of the kind in the heavens, and to which the discovery of its parallax by the late Professor HENDERSON has given a degree of astronomical importance no less conspicuous,—consists of two individuals, both of a high ruddy or orange colour, though that of the smaller is of a somewhat more sombre and brownish cast. They constitute together a star which to the naked eye is equal or somewhat superior to Arcturus in lustre." After describing the magnitude which he considered should be assigned to each, and which agrees more nearly with what I have already stated as being my own opinion, and after giving some optical and physiological reasons which may tend to explain the under-estimation of former observers,—Sir John then cites the fact of the remarkable amount of proper motion of the stars, and says, "This consideration alone suffices to decide us in admitting a binary connection between them, and it will therefore be interesting to see what evidence observation furnishes of orbital motion round their centre of gravity. For this, however, the data are somewhat precarious, as we have, until recently, only catalogued differences of A.R. and Polar distances, from which to calculate the angle of position and distance at the epochs of observation. This done, and the results tabulated, together with my own positions and distances, obtained by direct measurement with the equatorial, we have as follows:"—

Authority.	Epoch of Observation.	Position.	Distance.
Lacaille,	1750	218 44	20.51
(Maskelyne,	1761		15.5)
Fallowes,	1822	209 36	28.75
Brisbane,	1824	215 25	22.45
Dunlop,	1825	213 11	22.45
Johnson,	1830	215 2	19.95
Taylor,	1831	215 58	22.56
Herschel,	1834-68		17.43
	1834-79	218 30	
	1835-86	219 30	
	1837-34	220 42	
	1837-44		16.12



I have inserted here the observation of MASKELYNE in 1761, with which, probably, Sir J. HERSCHEL was unacquainted; it makes an apparently bad figure among the rest, but is by no means to be left out on that account merely, seeing the care and the superior means for that day with which the measures were made.

"Mr FALLOWES' determinations," continues Sir JOHN, "in this series, are open to objection, from the decidedly inadequate instrumental means by which they were furnished (a small altitude and azimuth circle). Mr TAYLOR's results also rest on so few observations, as to entitle them to little weight.

"Though it is obviously impracticable to deduce any elliptic elements from such a series, there are some features which it is impossible not to recognise. There can be no doubt that the distance has gone on decreasing since 1822 at least; and the comparison of the measures least open to objection leads us to conclude that, for the ten years previous to 1838, the rate of decrease was  $\frac{7}{13}$ , or a little more than half a second per annum, which, if continued, will bring on an occultation, or exceedingly close appulse, about the year 1867. The small amount of variation in the angle of position shews that the plane of orbital motion passes nearly, but not quite through our system, while its actual tendency to increase exemplifies the general law of increase of angular velocity, with diminution of distance. Mr FALLOWES' distance is probably too great by 3" or 4"; but in the long interval between 1750 and 1822 (at the former of which epochs the distance must have been on the increase), there is room for a very much greater excursion of the small star towards its apparent aphelion, so that, although we are sure that the major axis of the real orbit *must* materially exceed 24", it is impossible to say *how much* it may exceed that limit. Taking, therefore, the co-efficient of parallax for  $\alpha$  Centauri, as determined by Professor HENDERSON, at 1", it will follow from what has been said, that the real orbit of one star about the other cannot be so small as that of the orbit of Saturn about the sun, and exceeds, in all probability, that of the orbit of Uranus.

"The plane of the orbit in the case of  $\alpha$  Centauri, passing nearly through our system, my method of approximating to the elliptic elements becomes inapplicable, and for their determination, measures of the distance of the stars from each other can alone be relied on. No subject more worthy of continued and diligent inquiry can possibly be urged on the attention of southern astronomers."

Thus the result arrived at, both by Professor HENDERSON and by Sir J. HERSCHEL, and which, though proved since to be erroneous, would have been probably concluded by any one else from the same data, seems to be, that the smaller star had been employed during the last century in gaining its aphelion, without any sensible change of angle of position; what the aphelion distance, the diameter of the orbit, and the period of revolution, might be, no guess could be attempted: but in his address, on the occasion of giving the gold medal to BESSET for his discovery of the parallax of  $\delta$  Cygni, Sir JOHN HERSCHEL stated,



that the orbit of the smaller star of  $\alpha$  Centauri might subtend the large angle of about 1 minute. As it had been actually observed at an elongation of  $28''$  on one side of the large star, the very reasonable supposition of a nearly circular orbit, seen in profile, would, in course of time, give the same distance on the opposite side. Both authorities also predicted the probability of an appulse of the same stars somewhere about the year 1867.

At the time of Sir JOHN HERSCHEL going to press, he knew of no micrometrical measures subsequent to 1838, but soon after that period, most fortunately for the interests of sidereal astronomy, Captain JACOB came into the field. On visiting the Cape from India, where he had been engaged in the great Trigonometrical Survey, he spent most of his time at the Observatory, and not only witnessed, but took part in the parallax observations of  $\alpha$  Centauri. He then ordered a good achromatic telescope from Dollond, and on its arrival in India, after his return there, erected a small observatory, and devoted all his spare time with great perseverance and eminent success to that most difficult species of observation,—viz. the double stars.

About a year ago, he wrote to me to send him out all the old observations known of  $\alpha$  Centauri, for the two stars were approaching more and more rapidly, and his own observations seemed to give a most unexpected orbit. The first document which reached him was Professor HENDERSON's memoir on the parallax, and then Captain JACOB found that he had been forestalled as to the actual facts of an appulse being shortly to be expected, though he indeed fixed the time as being very much closer at hand, bringing it from 1867 to 1851; but as to the idea that the small star had only been gaining its aphelion, without sensible alteration of angle of position since 1751,—he found, on computing the orbit, that within that interval it had made a whole revolution, or had altered its angle of position by  $360^\circ$ . The subsequent arrival of Sir J. HERSCHEL's observations fully confirmed Captain JACOB's views, who has now recomputed the orbit, including all the known observations up to the present time; and though this performance is to be considered but a first approximation, still it will probably not be very much altered by future observations in any of the important elements.

The difficulty that might be started at the first mention of this new opinion, would be, that supposing the small star, instead of having remained almost stationary in its orbit for the last 100 years, to have really made a whole revolution,—how came it to pass that every observer in the interval saw it always in about the same position on the west, and never on the east of the large star? This objection is fully met by the extraordinary nature of the orbit, which turns out much more nearly like that of a comet than of a planet, the greatest distance being  $21.85''$  and the least  $0.5''$ , in consequence of which, the small star moves with such surpassing rapidity at its periaster, actually  $2^\circ 40'$  per day; that it is but a very short space of time on the eastern side of its primary, and when at its



aphaster on the west, moves again with proportionate slowness, and so is seen there for a long period with hardly any sensible alteration of place. The time of revolution seems to be as short as 77 years; and LACAILLE and MASKELYNE's<sup>1</sup> observations, which had before appeared somewhat anomalous, are fully reconciled, as belonging to a former revolution; indeed the small star seems to have been almost in precisely the same situation with respect to the large one when observed by MASKELYNE in 1761, as it appeared to SIR J. HERSCHEL in 1838; and had observations been continued for twelve years after MASKELYNE's time, our knowledge of sidereal astronomy might have been almost a century in advance of its present position.

*Captain W. S. Jacob's Observations of  $\alpha^1$  and  $\alpha^2$  Centauri (A.R.  $14^h 29^m 5^s$ , N.P.D.  $150^\circ 12'$ ), made at Poonah, Lat.  $18^\circ 31' N.$ , Long.  $4^h 55^m 42^s E.$ , with a Five Feet Achromatic Telescope.*

Angle of Position of the Two Stars.	Weight of Observations.	Number of Observations.	Magnifying Power.	Distance of the Two Stars.	Weight of Observations.	Number of Observations.	Magnifying Power.	Estimated Magnitudes.	Date.	Remarks.
230.1	8	4	87	11.03	9	4	87	1-2.5	1846, .17	flaring.
232.7	15	6	87	11.03	4	4	87	1-3	.20	do.
233.3	13	5	152	11.09	5	4	152	1-3	.20	do.
232.5	13	5	87	10.70	12	4	87	1-3	.26	definition tolerable.
232.2	12	5	87	10.12	8	4	87	1-3	.61	daylight; dawning.
234.1	21	7	87	9.47	19	6	87	1-3	.65	daylight; definition tolerable.
234.8	12	5	87	9.40	11	4	87	1-3	.97	do.
236.0	12	5	87	9.27	8	4	87	1-3	.99	do.
236.4	18	5	87	9.67	14	4	87	1-3	1847, .03	do. good.
236.0	17	5	87	9.30	18	4	87	1-3	.03	do. tolerable.
				9.35	14	4	87	1-3	.04	do. do.
234.7	12	5	152	9.00	10	4	152	1-3	.26	do. do.
233.6	12	5	87	9.47	11	4	87	1-3	.36	flaring.
234.0	14	5	152	9.64	11	4	152	1-3	.37	do.
235.9	16	5	152	9.81	13	4	152	1-3	.44	definition tolerable.
236.6	11	5	87	8.25	14	4	87	1-3	.93	daylight; definition tolerable.
237.1	12	5	87	8.25	8	4	87	1-3	.93	do. do.
238.0	18	5	152	7.96	13	4	152	1-3	.96	do. very good.
238.0	13	5	152	8.31	10	4	152	1-3	.97	do. do.
238.1	12	5	152	8.12	11	4	152	1-3	1848, .00	do. fair.
238.1	18	5	152	8.03	14	4	152	1-3	.00	do. excellent.
238.2	19	5	152						.01	do. do.
238.0	21	5	152	7.95	16	4	152	1-3	.01	do. do.
238.3	18	5	152	8.03	14	4	152	1-2.5	.02	do. good.
238.1	21	5	152	8.07	14	4	152	1-2.5	.04	do. do.
238.0	17	5	152	7.78	14	4	152	1-2.5	.05	do. do.
238.3	19	5	152	7.89	16	4	152	1-2.5	.05	do. slightly tremulous.



*Captain W. S. Jacob's Orbit of  $\alpha^1$  and  $^2$  Centauri.*

Position of perihelion,	$\pi = 26^\circ 24'$
Inclination to the plane of projection,	$\gamma = 47 \ 56$
Position of ascending node,	$\Omega = 86 \ 07$
Angular distance of perihelion from node on the plane of the orbit,	$\lambda = 291 \ 22$
Eccentricity,	$e = 0.950$
Epoch of perihelion passage,	$T = 1851.50 \text{ year}$
Periodic time,	$P = 77.0 \text{ years}$
Mean motion,	$n = 4^\circ.675$
Semixis major,	$a = 15.50''$
	Mass = $\frac{1}{4}$ of the Solar

*Apparent Orbit.*

Maximum distance,	$= 21.85''$ at $207.5^\circ$
Minimum, ...	$= 0.50 \dots 5.0$
Greatest daily motion,	$= 2^\circ 40'$

(See Plate XI.)

We thus have here altogether *one* of the most, if not *the* most, interesting and important sidereal system in the heavens; the only one which can compare with it is  $\gamma$  Virginis, and that has been looked upon as being amongst the double stars, what HALLEY's comet is amongst comets; but though so well and frequently observed of late years, it was not instrumentally measured so early as  $\alpha$  Centauri, and it is a much smaller star, with an orbit of only one-fourth the apparent dimensions, and a period of time double the length of its southern rival; so that, while the actual observation for the purpose of carrying theory with fact would be eight times more difficult in the case of  $\gamma$  Virginis, and loaded with eight times the probable error of observation, there is the further objection, that on account of the greater length of the period, but a small portion of the orbit could be determined by one observer, or even by one instrument.

But the crowning importance of the binary system of  $\alpha$  Centauri, is the accurate determination of its parallax or distance from us, by the late Professor HENDERSON, as we are thereby enabled to speak, not only of the proportions of the different parts of the orbit, but of their actual size, and the weight of the two bodies. Thus the least distance of these two suns is only half that of the earth from the sun, or a little less than that of Venus, while the greatest distance is a little more than that of Uranus; and the mass of the two stars comes out three-quarters of that of our sun, their distance from us being 226,100 times our distance from the sun.

Well, therefore, may Sir J. HERSCHEL have said, "that no subject more worthy of diligent and continued inquiry can possibly be urged on the attention of southern astronomers."



But the most interesting part of the orbit is still to come, viz., the periaster in 1851, and that this be well observed is indeed to be earnestly hoped, for the period will be an eminently crucial one; it proved so in the case of  $\gamma$  Virginis, imperatively requiring an excessive alteration in all the elements except one, as previously calculated; and in the case of  $\alpha$  Centauri, the characteristic features of the orbit are of a much more violently marked nature, besides being represented altogether on a larger scale.

The extreme importance of obtaining an abundance of observations at that epoch may be further indicated by the mere statement, that it cannot yet be considered as fully *proven*, that the law of gravity extends absolutely unaltered to the most distant parts of the sky, and the only mode of proof open to us is by observing the double stars. It is true that most of the orbits yet computed on the theory of gravity have turned out very near the truth, but still not quite so near, it must also be confessed, as could have been desired; and in the luciferous case of  $\gamma$  Virginis, every orbit that has been computed for it yet, has persisted in giving a minimum distance of not less than  $0.5''$ , while observation at the time of the periastral passage made it certainly much smaller.

I do not, of course, by any manner of means, wish to express any doubt on these grounds as to the sufficiency of gravity to explain all the observed phenomena; a great part of the *onus*, or the whole of it, may rest on the excessive difficulty of the species of observation, and their inappropriateness for calculation in all ordinary manners, caused by the extreme roughness of even the very best procurable data; resembling, indeed, those of the comet of 1556, whose return, calculated on such wretched notices of its former perihelion passage, we have been looking out for in vain so long.

But whatever weight we may attach to the insufficiency of our observations and methods of calculation,\* it is always proper to draw a distinct line of demarcation between those things which are proved and those which are merely inferred, and not seek to enjoy a triumph before the victory has been decidedly achieved.

\* In a letter just received from Captain JACOB, he says that he thinks he has fallen on the right orbit of  $\gamma$  Virginis at last, having obtained one that expresses all the known observations very well, and gives a minimum distance of  $0.23''$ .







XXXI.—*An Attempt to Improve the present Methods of Determining the Strength and Direction of the Wind at Sea.* By C. P. SMYTH, Esq., F.R.S.E., Professor of Astronomy in the University of Edinburgh. (With a Plate.)

(Read April 3 and 17, 1848.)

Last year, my friend Captain COCKBURN, R. N., brought to my notice the very lax method which is usually pursued at sea in determining the strength and direction of the wind; and said, that he had for many years been trying to contrive some sort of anemometer that might be useful on board, as well as an easy method of eliminating the effect of the motion of the ship on the true character of the wind, but hitherto without success. I undertook, therefore, to endeavour to supply him with these two desiderata. He thought that they would be useful, in a practical point of view, in seamanship; and as I considered that they might be of importance in meteorology, I was the more ready to lend my assistance.

The foundation of meteorology as a science, may be considered to reside in a knowledge of the general motions of the atmosphere; and these may be far more correctly determined at sea than on any station on land, where local circumstances always produce more or less of an artificial climate, circumscribed, perhaps, to a few miles, or even less, and therefore of no moment to the world at large.

But although a ship, traversing the uniform surface of the ocean, of nearly unvarying temperature, day and night, and winter and summer, is thus naturally under highly favourable circumstances for advancing the science, still those opportunities seem never to have been turned to full account.

The usual mode of entering the wind in the log-book used to be, and may be still in the greater part of the merchant navy, "a hard breeze, or a stiff breeze, or strong breezes, and squally," &c., &c.; each person judging by his feelings merely, and having a nomenclature of his own for those feelings; so that there is no way of reducing them all to any one uniform natural standard.

On account of the flagrant absurdity of this method, in a scientific point of view, Admiral BEAUFORT, of the Hydrographical Office, proposed and procured the general adoption of, in all Her Majesty's ships, a well-digested table of the names of different strengths of wind, and of the means of judging of them, in the terms of the numbers of which table all entries in the log-book were to be made.

*Admiral Beaufort's Wind-Table.*

0. Calm.		
1. Light air, .....	Or just sufficient to give steerage way.	
2. Light breeze, ...	Or that in which a well-conditioned man-of-war, with all sail set, and clean full, would go in smooth water, for	{ 1 to 2 knots. 3 to 4 do. 5 to 6 do.
3. Gentle breeze,....		
4. Moderate breeze,		



5. Fresh breeze, ...	} Or that to which she could just carry in chase, full and by	Royals, &c.
6. Strong breeze,		Single-reefed topsails and top-gallant-sails.
7. Moderate gale.		Double-reefed topsails, jib, &c.
8. Fresh gale, .....		Triple-reefed topsails, &c.
9. Strong gale, ...	} Or that in which she could scarcely bear close-reefed main-top-sail and reefed foresail.	Close-reefed topsails and courses.
10. Whole gale, ...		
11. Storm, .....	Or that which would reduce her to storm-staysails.	
12. Hurricane, .....	Or that which no canvass could withstand.	

But although this was at the time a great improvement on the old system, it is by no means sufficient for the requirements of the present day; for so much is still left to the feelings and experience of each observer, that one officer will say that the wind should be marked as No. 4; while his companion may say it is rather No. 5, and another may decide on 3 being the more appropriate expressive number.

But even supposing that they were all agreed on this point, and said the wind was 4 in strength, no one has ever attempted to determine what *that* number, or *any other* in the table, really means,—what natural strength of the wind, or what velocity of the air, it is equal to. A simple inspection of the table shews that the scale is by no means a uniform one; for, between Nos. 1 and 2, there can hardly be a difference of  $\frac{1}{2}$  lb pressure of the wind on the square foot; while between 11 and 12, there may be 20 or 30 lb difference.

Now, this is an imperfection in the system of the gravest kind, for if the strength of the apparent wind be not observed in such terms as are reducible to those in which the velocity of the ship is measured, the strength of the true wind, or that which a person would feel if perfectly at rest on the ocean, cannot be determined; and the real motions of the atmosphere would be concealed to a great and unknown extent, by the effects of the movement of the ship.

These defects are of consequence, too, even in ordinary practical matters, as in trial squadrons; for it is not the *absolute* speed of a ship which is wanted, but the *relative* speed of it, with regard to the wind; and the winds, blowing at the same time on the various ships several miles asunder, may be of very different strengths; as any one may prove to himself, by noting the capricious streaks, in which, after a calm, a change sets in on the surface of the water. It is true, that, by keeping the ships out a long time, a mean may be obtained of all these little atmospherical currents, but the result will not be satisfactory; and, as in the celebrated case of the three trial brigs, there may be a total difference of opinion on the absolute merits of each vessel, by reason of the cause of the apparent superiority, now of one, and now of another, not being properly understood.

These difficulties are all of the character which would be removed by an instrumental method of determining the strength of the wind; and this is not the first time that the use of an anemometer has been proposed on boardship; but those which have hitherto been tried would seem to have failed, from not having been of the appropriate kinds; and partly, indeed, because, in the case of those officers



with whom I have communicated, they seemed to look upon the effect of the motion of the ship as something insuperable, and in the face of which there was no need of aiming at any great accuracy.

On beginning to consider the best species of anemometer for the purpose in question, it appeared to me that something on the principle of the log-line used for determining the ship's speed through the water, would be appropriate; for, notwithstanding the very scientific and accurate character of numerous instruments invented for the same purpose in later years, still they have one by one disappeared, or been forgotten; and the old log-line has not only continued in existence from the earliest times to the present, but ninety-nine out of every hundred ships that now go to sea are furnished with it, and with it alone. This peculiar vitality and power of withstanding the changes of fashions and times, may perhaps depend partly on this, that the quantity to be observed is measured on so very large a scale, that the clumsiest person can read it off to sufficient accuracy; while, with the more modern methods, the accuracy of a person accustomed to delicate observation, is necessary for any trustworthy determination at all.

The case in anemometry, perfectly parallel to the log-line, would be,—to have a float of some sort suspended in the air, and to note how many feet of line it ran out in a certain length of time, under the combined influence of the movements of the air and the ship. But though so perfect an imitation as this is prevented by the rarity of the atmosphere, yet the vane of a horizontal windmill is an approach to the same thing; where the float is supported in the air on a horizontal arm fixed to a vertical axis; and the distance run out, is measured by noting the number of revolutions, and the magnitude of the circle described by the vane or float.

The small motive power, however, of a horizontal windmill, only one-twelfth, according to SMEATON, of the vertical construction, together with the necessity of having a moveable screen to cover up one-half of the wheel from the action of the wind, has prevented the adoption of such a machine as completely for scientific as for industrial purposes.

The vertical windmill, again, though it gains a far greater degree of mechanical power, is also inappropriate for our purpose, on account of the very different amounts of glancing off of the wind, at different velocities, from the inclined surface of the sail; the unavoidable twisting of the necessarily light arms, which prevents the angle of the sail being perfectly constant; and the impossibility of fixing one uniform standard for the shape, size, and angle of the sail; as well as the necessity of having the plane of the sail-wheel always turned toward the direction of the wind.

All these objections have, however, been very happily removed by a novel windmill, of the horizontal form, invented by Mr EDGEWORTH, which requires no screen, but revolves by virtue of the shape of the float-boards; which shape being a constant quantity in all strengths and directions of the wind, the revolution goes



on in the same direction from whatever quarter the wind may come, and increases in rapidity exactly in proportion to the strength of the wind.

Mr EDGEWORTH had proved many years ago the increased effect of wind on a concave surface to a flat one, by taking a sheet of tin, and shewing that when bent into so very concave a form as to present considerably less area than in its flat condition, to a current of wind blowing straight upon it, that still it experienced a greater degree of pressure. But it was only very recently that he carried the principle farther into a practical form; and the first notice of this is found in Dr ROBINSON's communication to the British Association at Southampton, descriptive of the application to a Whewell's anemometer of one Mr EDGEWORTH's horizontal vane wheels, where each vane consisted of a hemisphere, and the concavities being all turned in one direction, and experiencing one-third more resistance than the convex sides, the whole revolves from the concave as it were to the convex sides, at one-third the rate of the wind.

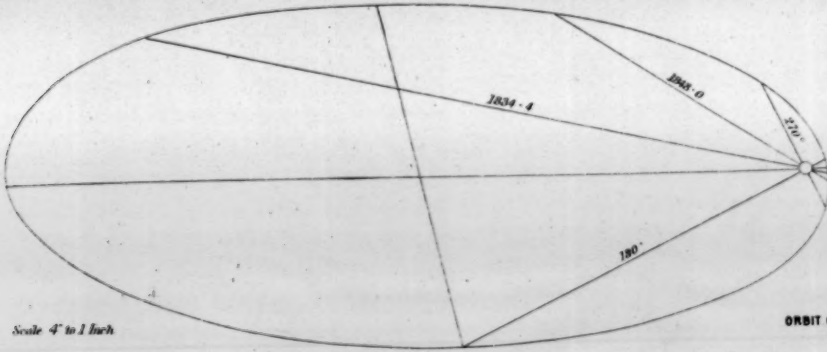
This, then, seemed to be eminently the sort of anemometer for use on board-ship.

No particulars of size or construction were given, only the important principle involved was mentioned; and as the first instrument which I had made, did not prove sufficiently sensitive, I entered on a course of experiments to ascertain the best sizes of the machine, and shape of the floats; and being greatly assisted therein by the practical skill and ingenious methods of Mr MILNE, the artist employed, was at last enabled to fix definitively on the instrument figured in the accompanying plate as the one which combines the greatest number of advantages, and forms altogether the best standard, perhaps, that can be adopted.

There are 4 hemispherical floats, 4 inches each in diameter, and 1 foot apart from centre to centre: an endless screw, on the axis of the vane-wheel, gives motion to a train of wheels and pinions, which serve to measure the number of revolutions made;  $1\frac{1}{2}$  grain, in the centre of one of the floats, is sufficient to produce motion. (See Plate XI.)

If the instrument be made on too small a scale, then it will have to overcome so much larger a proportion of the friction of surface than a larger one, that the floats will not move at one-third the velocity of the wind; but as much of this friction and resistance depends on the linear measure of the parts, while the motive power, which is as the area of the float, increases as the square of the dimensions, it is evident that increased velocity may be obtained by adopting a larger instrument. There is, however, a danger of passing the proper medium again in this way; for, as some of the sources of friction increase according to the *weight* of the moving parts, or as the *cube* of the linear dimensions, these may soon surpass the motive power, which increases as the *square* only. There is another objection also to having a vane-wheel with much mass, or *vis inertiae*; for although we wish in this inquiry to get a mean, or the total sum, of all the little separate gusts of

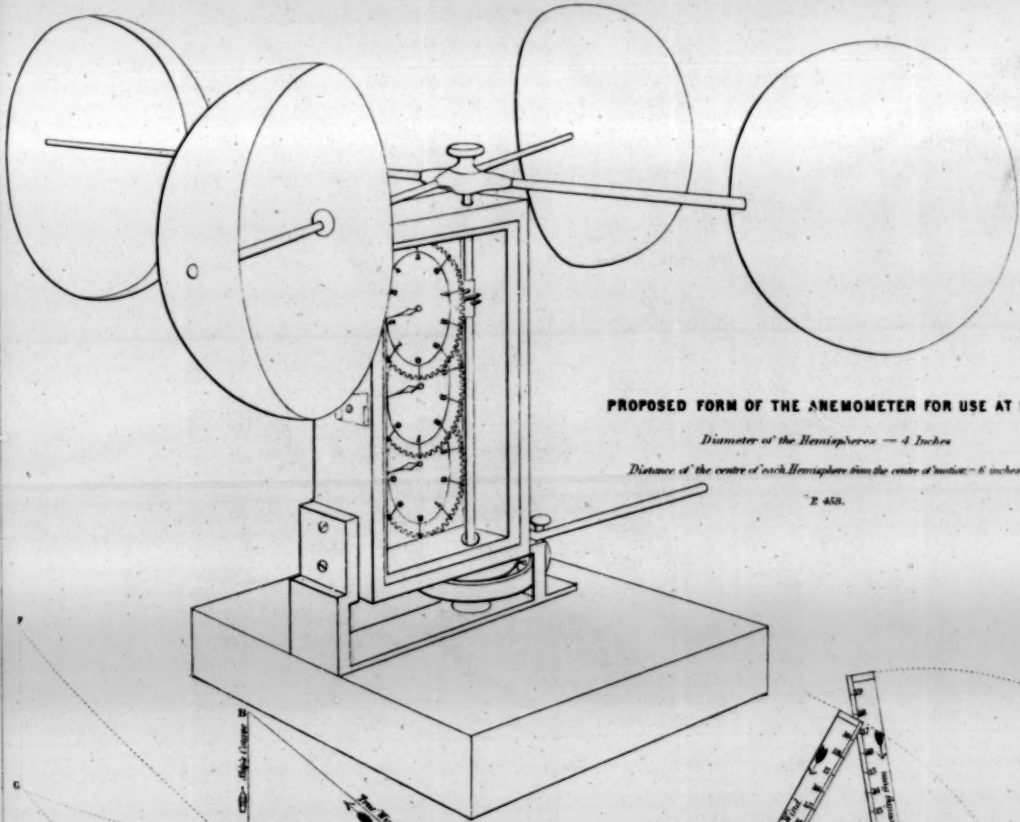




Scale 4" to 1 inch

ORBIT OF  $\alpha$  CENTAURI.

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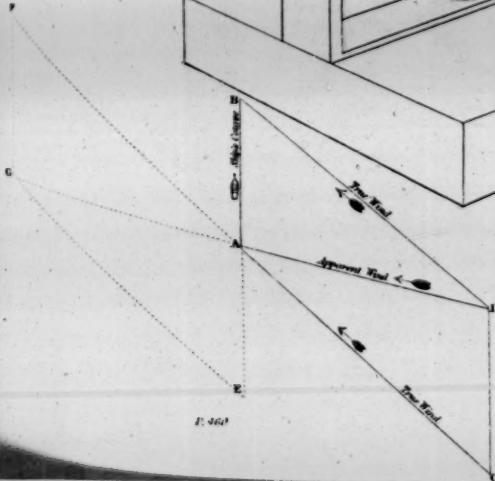


PROPOSED FORM OF THE ANEMOMETER FOR USE AT SEA

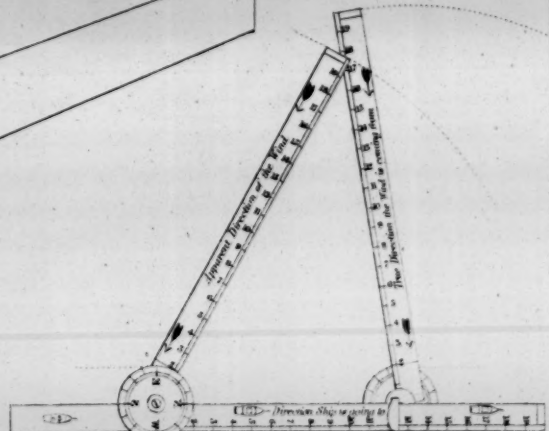
Diameter of the Hemispheres — 4 Inches

Distance of the centre of each Hemisphere from the centre of rotation — 6 inches

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P. 464.









which any particular wind is made up ; and although, in a mere mechanical point of view, a wheel of great weight would tend to equalize and mean all the currents of different intensity, still it can only do so with a certain amount of loss, and with the total omission of all very light impulses ; and the only way accurately to sum up all those separate little quantities, is to employ an instrument which shall be as sensible as a feather, and take full and *immediate* account of the slightest motion of the atmosphere.

After trial of floats 2, 3, 3½, 4, and 6, inches in diameter, the 4-inch ones were considered as being the best ; and the hemispherical shape was also preferred, as giving the greatest per centage of velocity with the least weight of material and smallest side resistance, as well as offering the shape, of all others, of the easiest and truest execution, and best understood everywhere.

Various experiments were tried, of making the floats more or less conical, in order to diminish the pressure of the wind on their backs ; but though that point was most eminently obtained, still the advantage was outweighed by the necessary increase of weight accompanying the increase of surface, the greater side resistance to the wind, and the diminished pressure on the concave side.

In the month of January this year, I had the opportunity of trying the value of the revolutions of this anemometer, in company with Captain COCKBURN. The instrument was mounted on the top of a cab, clear of the driver's head, and driven at a pretty uniform speed of above seven miles an hour, first forwards and then back, on two miles of the London Road ; the object being to measure the artificial wind produced by the motion of the vehicle, which would of course be equal to a natural wind blowing with the same velocity in the contrary direction. The first day there was a rather strong breeze, which would have completely vitiated the experiments, but that, as it was blowing almost exactly in the direction of that part of the road which was traversed, we expected to be able to eliminate its effects by taking a mean of the numbers given in going and returning.

When going, having the wind with us, the instrument, which measured then only the difference between the velocities of the wind and the cab, made 209 revolutions in one mile ; but in returning, measuring the sum, it gave 921 revolutions in the same distance. The mean of these, or 565, when multiplied by 3·1415 feet, or the space described by the centre of the float in one revolution, gives a velocity not exactly  $\frac{1}{3}$ , but  $\frac{1}{2\cdot974}$  of that of the wind.

The second day was all but perfectly calm ; it was at the commencement of the long-continued frosty weather ; and a proof of the general stillness of the air was offered in the dense, unnatural manner in which the smoke was accumulated and remained suspended over the city. In going out, 558 revolutions were made in one mile ; and in coming back, 551. The mean of these, or 555, gives a velocity



of the floats of  $\frac{1}{3.028}$ ; and the mean of both days makes it  $\frac{1}{3.001}$ , or almost exactly what Dr ROBINSON stated that it should be from theoretical investigation.

The result was, so far, perfectly satisfactory, and seemed to shew that the instrument was fully entitled to be tried at sea, as giving a good and convenient measure of the velocity of the wind. The particular proportion mentioned ( $\frac{1}{3}$ ) might probably not obtain equally under all velocities of wind, but it has not been thought worth while to try the instrument at other velocities on shore; because there are much more powerfully modifying circumstances in the rolling motion of the ship, the full effect of which can only be determined by actual experiment at sea. But whatever alteration of the value of the revolutions takes place under such conditions, naval officers may be assured of this, that a certain physical connection between the velocity of the air and the revolutions of the anemometer exists, and its exact nature may be easily investigated and discovered, and the strength of the wind may then be entered in the log-book, in numbers expressive of the velocity of the air in knots per hour, or in the same terms as the motion of the vessel; and as the direction of the wind is already sufficiently well observed by the different vanes at present in use on board ship, all the elements of the *apparent* wind may, with the assistance of this anemometer, be looked upon as satisfactorily obtained.

This apparent wind being, however, the combined effect of the motions of the ship and of the air, may be very different from the true wind, both in direction and in strength. When the ship is going with the wind, the velocity of the true wind will be equal to the sum of the velocities of the ship and of the apparent wind; and when going against the wind it will be equal to their difference, without alteration of direction in either instance. But in almost every other possible case both the velocity and the direction will be changed, the problem being a particular application of the well known and important theorem in mechanics of the parallelogram of forces; the velocity of the ship observed forming one side, the velocity of the apparent wind—also obtained from observation—being the diagonal, and the true wind to be determined, another side.

This may be illustrated familiarly as follows:—Let the line A B (Plate XI.) represent the motion of the ship, the length of the line shewing the velocity in knots per hour as determined by the log-line, and the position of the line shewing the vessel's course, or the direction *to which* the vessel is proceeding, obtained by reference to the vanes and the compass. Similarly, let the lines A C or B D represent the true wind, or the wind which a person at rest would feel to be blowing over the sea during the time that the ship passed from A to B. The length of the lines A C and B D shew the velocity of the wind in knots per hour, given by the anemometer, and the position of the lines gives the direction *from which* the wind is coming.

Under such circumstances, what will be the apparent wind, or, in other words,



what will be the direction and the velocity of the wind which a person in the ship will feel?

Now, the motion of the ship from A to B being equivalent to a wind moving with equal velocity in a contrary direction, or from B to A, then any particle of air at rest at A will be driven, if acted on by the impact of this adventitious wind only, to a distance, equal to A B, beyond A, and in the same direction, or to E; but if acted on only by the natural wind, the particle will receive a velocity and a direction equal to that, and be driven from A to F; but as the particle is acted on instantaneously by both forces, it will neither go to E nor to F, but in an intermediate direction, and closer to one or other according to the relative strength to the two forces, or in the diagonal of the parallelogram of which A F and A E form two sides. A G, therefore, in the parallelogram A E F G, represents, by its length and position, the distance to which, and the direction in which, a particle at A will be driven under the united influence of the natural wind blowing over the sea, and the artificial wind caused by the motion of the ship; *i. e.*, A G represents the apparent wind, or that which a sailor would observe.

For convenience of illustration we may complete the parallelogram A B D C, which is similar to the parallelogram A E F G, and where A D is consequently equal to A G; and we may now, for the purposes of calculation, omit all but the triangle A B D, in which the sides A B, A D, being given by observation, and the included angle B A D being obtained from the difference of the observed directions of the ship and of the apparent wind, we have merely to compute by the usual rules for plane triangles, the length of the side B D, or the velocity of the true wind; and the angle A B D, which, being added on to the course of the ship, gives the direction of the true wind.

Considering, however, the necessary length of time which such a computation must occupy in the hands even of the most expert (the mere preparation of the angles for computation would of itself be no small matter, on account of the rough character of the subtraction of the course of the ship from the direction of the wind—both observed by compass points—the reduction of this to degrees, then the re-reduction of the resulting angle into points, and the addition of them to the course of the ship): considering, also, the almost infinite number of times the calculations would have to be gone through in any voyage, and the extreme improbability of any amateur undertaking so large a quantity of an unimproving sort of labour, I have had a set of scales made for solving the problem by inspection, and the entry being made with the velocities and *directions* observed, the velocity and *direction* of the true wind are immediately given.

These scales, which are represented in Plate XI., are formed of two ordinary jointed rulers, having moveable circles marked with the points of the compass on the joints, and three sets of divisions on the legs, to include all possible velocities



of the wind and ship, from 1 mile to 100 per hour, each mile being capable of subdivision into tenths.

A leg of each scale being made to slide one upon another, with the joint of each turned outwards, the centres of these joints are to be placed at such a distance apart as corresponds to the velocity of the ship in terms of any one of the three sets of divisions on the legs. Both circles are then turned, so as to shew on one edge of that double leg the observed direction of the ship's course; the single projecting leg of one scale being then placed in the observed direction of the apparent wind, and the projecting leg of the other moved until one edge of it cuts on the first, the divisions indicating the velocity of the apparent wind; then the length of the intercepted portion of that second leg shews the velocity of the true wind, and its reading on its own circle gives the direction.

The circles are graduated to degrees as well as to points of the compass, so as to be capable of solving all ordinary cases of plane triangles, as well as those immediately contemplated, and to suit the instances sometimes found of the more exact determination of the direction of the wind in degrees instead of points.

As the scales stand at present, they require, when the significant numbers of the anemometer shall have superseded the present unmeaning ones entered in a ship's log, no new data from observation; but by merely running down, scale in hand, the columns of "Directions and Velocities of the Ship, and Apparent Wind," as entered in the book for the ordinary purposes of navigation, the direction and velocity of the true wind may be rapidly entered in a couple of adjacent columns; and the importance of making this correction before beginning to reason, from the data at present afforded by ships, on the general character of the winds on the surface of the ocean, may be seen in the accompanying supposed extract from the journal of a man-of-war or a steamer; where, though the true wind was the same during the whole interval, yet, on account of the different courses pursued, and velocities attained, by the ship at the various hours, the wind did alter to those on board at times, almost of 90° in direction, and from 9 knots to 23 knots in velocity.

Date.		Ship's		Apparent Wind.		True Wind.	
1848.	Hour.	Course (to)	Velocity.	Direction (from)	Velocity.	Direction (from)	Velocity.
April 17	1	N.	Knots. 10.5	WSW.	Knots. 12.1	SW. by S.	19.3
...	2	NNE.	10.4	SW.	9.3	SW. by S.	19.3
...	3	NE.	10.0	SSW.	9.7	SW. by S.	19.3
...	4	E. by N.	11.5	S.	14.0	SW. by S.	19.3
...	5	ESE.	11.8	S.	19.9	SW. by S.	19.3
...	6	SSE.	5.2	SSW.	23.3	SW. by S.	19.3
...	7	W.	4.1	SW.	22.6	SW. by S.	19.3
...	8	WNW.	5.8	SW.	21.8	SW. by S.	19.3
...	9	NW.	8.4	SW. by W.	19.3	SW. by S.	19.3
...	10	NW. by N.	14.0	W. by S.	18.7	SW. by S.	19.3
...	11	N. by W.	10.0	WSW.	14.1	SW. by S.	19.3
...	12	WSW.	3.3	SW. by S.	22.8	SW. by S.	19.3



XXXII. *On the Products of the Destructive Distillation of Animal Substances.*

Part I. By THOMAS ANDERSON, Esq., M.D.

(Read 3d April 1848.)

In April 1846, I communicated to the Royal Society a paper on a new organic base, to which I gave the name of Picoline, and which occurs in coal-tar, associated with the Pyrrol, Kyanol, and Leukol of RUNGE. In that paper I pointed out that the properties of picoline resembled, in many respects, those of a base which UNVERDORBEN had previously extracted from DIPPEL's animal oil, and described under the name of Odorine; and more especially mentioned their solubility in water, and property of forming crystallisable salts with chloride of gold, as characters in which these substances approximated very closely to one another. And further, I detailed a few experiments on the odorine of UNVERDORBEN extracted from DIPPEL's oil, with the view of ascertaining whether or not they were actually identical, but on too small a scale to admit of a definite solution of the question.

These observations, coupled with the doubts which had been expressed by some chemists, and more especially by REICHENBACH, as to the existence of the bases described by UNVERDORBEN, induced me to take up the whole subject of the products of the destructive distillation of animal substances, which has not yet been investigated in a manner suited to the requirements of modern chemistry. In fact, UNVERDORBEN is the only person who has examined them at all, and his experiments, contained in the 8th and 11th volumes of POGGENDORF's *Annalen*, constitute the whole amount of our knowledge on the subject; and his observations, though valuable, and containing perhaps as much as could easily be determined at the time he wrote, are crude and imperfect, when we come to compare them with those which the present state of the science demands. Since his time, the methods of investigation in organic chemistry have undergone an entire change: the simplifications of the process of organic analysis had not then been made, or at least had not come into daily use as the auxiliary of investigation, and UNVERDORBEN, who belonged to the old school, and contented himself with the observation of reactions only, was necessarily led, as I shall afterwards more particularly shew, to confound together substances, the reactions of which approximate so closely that it is impossible, or at least very difficult, to distinguish them by such means alone. The errors, however, lay with the method, and not with the observer; for UNVERDORBEN's experiments, so far as they go, I have found to



be correct in the main, notwithstanding their having been called in question by REICHENBACH, whose numerous researches on the kindred subject of the products of the destructive distillation of vegetable substances, gave weight to his opinion, and have indeed been the principal cause of the doubts expressed by others on the subject.

The investigation of these products has occupied me pretty continuously since the publication of the paper before alluded to; and my researches have now extended themselves over a large part of the subject, although, from its branching off into so many subdivisions, and embracing the consideration of so large a number of substances belonging to almost every class of organic compounds, some time must still elapse before it is complete in all its parts. It is my intention, therefore, as the subject naturally divides itself into several sections, to take up the consideration of these in a succession of papers, of which the present is the first, and in which I propose to consider the general properties of the crude product employed in my experiments, and those of certain of the organic bases contained in it.

The products of the destructive distillation of animal matters were long since employed in medicine, and were obtained from all parts of the body, and from almost every section of the animal kingdom; but these afterwards entirely gave way to the *Oleum Cornu Cervi*, which, as hartshorn is entirely free from fatty matters, must necessarily be the pure product of decomposition of the gelatinous tissues. The more volatile portions of this oil, separated by distillation with water, and purified by numerous rectifications, constituted the *Oleum Animale Dippellii* of the older pharmacopœias. These substances would, in all probability, have been the most convenient crude materials for my experiments; but as they have long since ceased to be employed, and cannot now be obtained except by going through the tedious and disagreeable process for their preparation, I have made use of the bone-oil of commerce, which is prepared on the large scale by the distillation of bones in iron cylinders, and can be had in any quantity from the manufacturers of ivory-black. This oil appears to differ in no respect from the true *Oleum Cornu Cervi*, and, like it, is the product of decomposition of the gelatinous tissues only; for previous to distillation the bones are boiled in a large quantity of water, by which means both the fatty matters and also a certain proportion of the gelatine are separated. They are then dried, packed in the cylinders, and distilled at a heat which is gradually raised to redness. The oily product of this distillation is separated from the watery portion, and, after rectification, forms the bone-oil of commerce; though in some instances this latter distillation is dispensed with, and the product of the first made use of without any further purification.

Bone-oil, as supplied by the manufacturer, has a dark-brown, almost black colour, with a somewhat greenish shade, and perfectly opaque in the mass; but when



spread in a thin layer on a glass plate, it is seen to be brown by transmitted light. Its specific gravity is about 0.970. Its smell is peculiarly disagreeable, and is mixed with that of ammonia, which is always present, though sometimes in so small quantity that its odour is disguised by that of the oil itself, and is only rendered apparent by distillation. A piece of fir-wood moistened with hydrochloric acid, and held over the mouth of a vessel containing it, rapidly acquires the dark reddish-purple colour which is characteristic of the pyrrol of RUNGE. Acids agitated with the oil acquire a brown colour, especially on standing, and extract the bases contained in it; but if the quantity of the acid be large, and in a pretty concentrated state, a nonbasic oil is also dissolved, which, on standing for some time, and more rapidly if heated, undergoes decomposition, and the fluid becomes filled with orange-yellow flocks of a resinous substance, which acquires a dark colour by exposure to the air; this change is produced by the stronger vegetable as well as the mineral acids. Alkalies extract an acid oil, and a considerable quantity of hydrocyanic acid, which, on the addition of an acid to the alkaline solution, and distillation, can be distinguished in the product by its smell, as well as by its reaction with the salts of iron.

Previous to the separation of the bases, the crude oil was again rectified in portions of about fifteen pounds each, in an iron retort,—an operation attended with some trouble, as the fluid is apt to froth up and boil over in the early part of the process, so that the retort must not be more than half full, and the heat requires to be applied in a very gradual manner. At first a watery fluid distils, containing in solution ammonia, and a small quantity of the most volatile bases. This is accompanied by an oil of a pale yellow colour, limpid and very volatile, which after a time comes over without water, and with an increased though by no means dark colour. The distillation proceeds in a perfectly steady and gradual manner, until about two-fifths of the oil have passed over, when a point is attained at which the temperature requires to be considerably raised, in order that the distillation may continue uniformly, and the product becomes much thicker and more oily in its appearance. At this point the receiver was changed for the purpose of collecting the less volatile portion apart, and the distillation continued until the bottom of the retort reached a red heat. The latter portions of these products were obviously altered during the distillation, for a bulky porous charcoal remained in the retort; the oil which passed over smelt strongly of ammonia, crystals of carbonate of ammonia made their appearance in the neck of the retort, and a certain quantity of water collected in the receiver. The oil also became gradually darker in colour, and more viscid in its consistence. By collecting in a succession of receivers, I had an opportunity of observing a great number of curious optical phenomena at different epochs of the distillation. The oils frequently presented well-marked appearances of epipolic dispersion, and the very last portion exhibited a curious species of dichroism, its colour being dark reddish-



brown by transmitted, and green, with the effect of opacity, by reflected light. All these appearances, however, were very evanescent, and are only seen in the newly distilled oil, for after a few days it becomes very dark coloured, and they are then no longer visible.

Both the more and the less volatile oils contain a variety of bases, and were separately treated for their extraction. In neither, however, is the quantity large. I obtained from the more volatile portion of three hundred pounds of bone-oil less than two pounds of the mixed bases; but as, in the course of the various processes to which it was submitted, some small portions were lost, the whole may perhaps amount to about three-fourths per cent. of the total quantity of oil. The less volatile portion yields a larger quantity, which may be estimated at two or three per cent. of the crude oil. These, of course, are only rough estimates, but they may serve to give an idea of the quantity of the products.

#### *Preparation of the Bases.*

For the preparation of the bases precisely the same processes were followed throughout for both portions into which the oil was separated by distillation; and as the bases to be described in the present paper were contained in the more volatile portion, I shall detail the steps followed in reference to that quantity only. The oil was mixed in a cask with sulphuric acid diluted with about ten times its weight of water, and the fluids left in contact for a week or two, during which time they were frequently agitated. More water was then added, and the whole drawn off, and the process repeated with fresh quantities of sulphuric acid as long as any bases were extracted. The solution, which had a reddish and sometimes very dark brown colour, contained the bases, along with a quantity of nonbasic oil and of pyrrol. It was mixed with an additional quantity of sulphuric acid, introduced into a glass distilling apparatus, and heat applied. As the fluid approached the boiling point, a quantity of the red resinous matter before alluded to began to separate, and occasioned succussions of so violent a character as to endanger the safety of the vessel, and render it necessary to interrupt the process for the purpose of filtering it off, after which the distillation proceeded without difficulty. A small quantity of oil distilled over, and the water which accompanied it had exactly the smell of the water in a gas-meter, and contained pyrrol,\* which continued to pass over for a long time, during the whole of which the distillation was continued. This distillation I had recourse to at first, from a suspicion that some of the bases were separated from the acid, and volatilised during the process; but so soon as I had ascertained that this was not the case it was

\* These odours were so exactly alike, that I was induced to seek for pyrrol in the water of gas-meters, and I found that when mixed with sulphuric acid and distilled, the product gave the characteristic reaction of pyrrol with fir-wood. Ammonia remained in combination with the sulphuric acid.



dispensed with, and the fluid boiled down in porcelain or copper evaporating basins, water being added, and the distillation continued until, by taking a small quantity of the fluid and distilling off a few drops in a retort, they were found to be free from pyrrol. Even this precaution soon became unnecessary, for a little experience enabled me to know when the evaporation had been sufficiently prolonged.

The dark-brown fluid which remained in the basins was once more strained, in order to get rid of such resinous matters as might have separated during the evaporation, and then distilled in a large glass balloon connected with a condenser, after the acid had been previously supersaturated by a base. For this purpose, potass, soda, and lime were indifferently made use of: the latter answers extremely well, but, owing to the large quantity of sulphate of lime separated, the distillation requires to be carried on in the chloride of calcium or oil bath. When the alkali is added in sufficient quantity, an oil floats up to the surface of the fluid, and a strong pungent odour is given off, in which that of ammonia is apparent, along with another which can be compared to nothing but the smell of stinking lobsters. At the first part of the distillation a transparent and colourless watery fluid passed over, which contained the bases in solution; but after this had continued for some time, an oil made its appearance running in globules down the tube of the condenser, and dissolving immediately in the fluid which had already distilled. When the bases ceased to distil in quantity, the receiver was changed, and a small quantity of oil heavier than water was obtained by continuing the distillation for some time. At the end of the process an oil remained floating upon the concentrated fluid in the balloon, the quantity of which is very variable, and depends on the distillation of the crude bone-oil, having been continued too long before changing the receiver. In fact, it contains some of the bases of the less volatile oil, and will come to be considered in an after part of the investigation.

To the product of the distillation sticks of caustic potass were added, and, as these dissolved, the oily bases separated from the fluid in a manner exactly similar to that which was observed in the preparation of picoline, as detailed in the paper to which reference has already been made. The alkaline solution was drawn off by means of a siphon, and more potass added as long as water was separated. In this way the greater part of the base was obtained, but a small quantity of the most volatile of all still remains in the alkaline solution, and cannot be separated except by the addition of a very large quantity of potass. It was, however, readily obtained by distilling the fluid, and collecting only the first portion of the product, from which it was separated by a comparatively small expenditure of potass. The small quantity so obtained was preserved separately from the large mass.



The product of this operation was found to be extremely complex, and to consist of a mixture of four or five different bases, exclusive of ammonia. For the purpose of obtaining these in a separate state a great variety of processes was attempted, but none were found to answer so well as fractionated distillation, although it is an extremely tedious method of separation, and occasions a considerable loss of substance, which is very annoying when the quantities obtained are so small. When the mixed bases were distilled with a thermometer, ammonia began to escape at a very low temperature; but at 160° Fahr. the fluid entered into steady ebullition, and a perfectly transparent and limpid oil began to distil. A small quantity of oil passed over between this temperature and 212°, which was received by itself, and the after products collected in a succession of receivers, which were changed at every ten degrees which the thermometer rose. The fluid continued in steady and rapid ebullition, and the thermometer ascended rapidly to 240°; and between that and 250° a considerable quantity was collected. It then again went up pretty rapidly, and another large quantity was obtained between 270° and 280°; after which the distillation proceeded more slowly until the temperature rose to 305°, at which point the characters of the products underwent a complete change. All the substances obtained at lower temperatures dissolved instantaneously in water; but that which now distilled floated on the surface, and only dissolved on agitation with a considerable quantity of water. Distillation now continued with somewhat greater rapidity, till the thermometer rose to about 355°, when a drop of the product allowed to fall into a solution of chloride of lime immediately gave the reaction of aniline. When this was observed, the whole remaining products, which formed only a small fraction of the whole, were collected together. They consisted chiefly of aniline.

The products of these different distillations were repeatedly rectified, and by this means bases were obtained, corresponding to the points at which the thermometer was found to remain longest in the first distillation. Of these I have as yet examined only the most volatile, and that which boiled at about 270°.

#### *Petinine.*

The most volatile portion of the bases obtained by the fractionated distillation, was mixed with the small portion which was separated with difficulty from the potash solution, and had been kept separate from the large quantity. The mixed fluid still contained a large quantity of ammonia, for the separation of which it was again rectified several times in succession, and fractionated in a small retort, the receiver being kept carefully cool. After this process has been repeated until it is properly purified, it constitutes the base to which I give the name of Petinine (from *περνιος*, *volatilis*), in allusion to its volatility, which is greater than that of any base yet known, with the exception, of course, of ammonia. The quantity of this substance contained in the bone-oil is excessively small, as I obtained from



three hundred pounds no more than was sufficient for the determination of its constitution, and the leading characters of a few of its compounds. It is probable, however, that some loss was incurred in the preliminary processes, as, from not anticipating the presence of so volatile a base, I did not take any precautions for producing complete condensation of the products, by means of freezing mixtures or otherwise; and a considerable quantity was also lost owing to my anxiety to expel completely the ammonia which it might retain.

*Constitution of Petinine.*

The petinine employed for analysis was very carefully dried over caustic potass, the fluid poured off after some days' contact, and distilled in the water-bath at a very gentle heat; a precaution which is rendered necessary by its dissolving a certain quantity of potass. I did not possess a sufficient quantity to make a determination of the nitrogen, but took it for granted that oxygen was absent; an assumption which is justified by the analogy of all the other volatile bases, as well as by the perfect coincidence of the experimental results with the calculated formulæ. It was analysed with oxide of copper in a very long tube, and gave the following results:

{	6.663	grains of petinine gave
	16.286	... carbonic acid, and
	8.382	... water;

corresponding exactly with the formula  $C_8H_{10}N$ , as is shewn by the following comparison:

Experiment.		Calculation.		
Carbon,	. . . 66.66	66.66	$C_8$	600.0
Hydrogen,	. . . 13.97	13.88	$H_{10}$	125.0
Nitrogen,	. . . 19.37	19.44	N	175.0
	100.00	100.00		900.0

In order to ascertain the atomic weight of petinine, I prepared its compound with chloride of platinum, and made the following determinations of the platinum contained in it:

- I. { 6.351 grains of chloride of platinum and petinine gave  
2.245 ... platinum = 35.34 per cent.
- II. { 3.860 grains of chloride of platinum and petinine gave  
1.372 ... platinum = 35.54 per cent.
- III. { 2.844 grains of chloride of platinum and petinine gave  
1.010 ... platinum = 35.51 per cent.



The atomic weights deduced from which agree very closely with the calculated results:

I. Atomic weight, by experiment,	910.3
II. ... ..	891.2
III. ... ..	894.2
Mean, . . . . .	898.5
Calculation, . . . . .	900.0

The mode in which this base is formed during the decomposition of gelatine, it is, of course, impossible at present to perceive. In its chemical relations it is, however, in all probability, related to the butyric series; and it is even possible that we may obtain it by artificial processes. Some time since, KOLBE\* published some researches on the galvanic decomposition of valerianic acid, among the products of which he discovered a carbo-hydrogen, having the formula  $C_8H_9$ . Now, by treating this substance in the same manner as benzene is acted upon for the preparation of aniline, we ought to obtain from it, if not petinine, at least an isomeric compound, as may be easily seen by comparing the formulæ of the different substances:

Benzene, . . . .	$C_{12}H_6$	$C_8H_9$	KOLBE's carbo-hydrogen.
Nitro-benzide, .	$C_{12}H_5(NO_4)$	$C_8H_8(NO_4)$	Action of nitric acid.
Aniline, . . . .	$C_{12}H_7N$	$C_8H_{10}N$	Petinine.

I have not yet had an opportunity of determining whether the change which theory would lead us to expect actually takes place, but there is every reason to suppose that it would.

#### *Properties of Petinine.*

Petinine is a transparent colourless fluid, limpid as ether, and possessing a high refracting power. It has an excessively pungent odour resembling that of ammonia, and yet quite distinct, for when the effect of its pungency has gone off, or it is smelt in a dilute state, its smell is disagreeable, and somewhat similar to that of decayed apples. Its taste is hot and very pungent. It boils at a temperature of about  $175^\circ F.$ ; but the quantity which I possessed was too small to admit of an accurate determination either of this point, or of its specific gravity, although the latter is certainly less than that of water. Petinine is a very powerful base, and immediately restores the blue colour of reddened litmus, and gives abundant fumes, when a rod dipped in hydrochloric acid is held over it. It unites with the concentrated acids, with the evolution of much heat. It dissolves in all proportions in water, alcohol, ether, and the oils; and is also soluble in dilute solution of potass, but not in concentrated. Petinine gives double salts with bichloride of

\* Memoirs of the Chemical Society of London, Part xxi.



platinum and corrosive sublimate, both of which are soluble in water. With chloride of gold it gives a pale yellow precipitate, which does not dissolve on boiling the solution, and is not deposited in crystals. Petinine throws down peroxide of iron from its compounds. It also precipitates salts of copper, and the oxide thrown down dissolves in excess of the base with a fine blue colour.

These properties agree with those of none of the bases described by UNVERDORFEN; and, in fact, it is certain that petinine could not have been present in the mixture to which he applies the name of odorine, for he expressly states that it commenced boiling at  $212^{\circ}$ . And it is easy to see why he did not obtain it, because, in separating the bases from the acid by which they were extracted from the crude oil, he took care to add a quantity of potass just so great that the oily bases were liberated, and not the ammonia; and as his object in doing so was to get rid of the latter substance, and there being no means of doing this exactly, it is probable that he did not fully separate the bases, but the most volatile, which is also the most powerful, remained in combination with the acid along with the ammonia.

#### *Compounds of Petinine.*

The minute quantity of petinine which I obtained has necessitated a very cursory examination of its salts, which are interesting, both from the facility with which they crystallise, and their great stability. None of them undergo change in the air, but may be left exposed for any length of time without acquiring colour. They are all soluble in water, and those with the volatile acids sublime without decomposing, and are deposited in crystals upon cold surfaces.

*Sulphate of Petinine*, is obtained by adding petinine to dilute sulphuric acid until the fluid is neutral. On evaporating, petinine is given off, and the solution, when concentrated to a syrup, concretes on cooling into a foliated mass of crystals of an acid sulphate. These crystals are strongly acid to test-paper, extremely soluble in water, and slightly deliquescent in moist air.

*Nitrate of Petinine*.—The solution of petinine in nitric acid, evaporated to dryness, and gently heated on the sand-bath, gives a sublimate of the nitrate in fine woolly crystals.

*Hydrochlorate of Petinine*.—Hydrochloric acid combines with dry petinine, with the evolution of much heat, and the formation of a salt which is extremely soluble in water, and sublimes in fine needle-shaped crystals.

*Chloride of Platinum and Petinine*.—If bichloride of platinum be added to a dilute solution of hydrochlorate of petinine, the salt formed remains in solution; but when both substances are concentrated, it falls as a pale yellow precipitate, which was purified by crystallisation from hot water. On cooling, the fluid, if sufficiently concentrated, becomes entirely filled with exceedingly beautiful golden-yellow plates, resembling those of crystallised iodide of lead. It is pretty soluble



in cold water, extremely so in hot, and is not decomposed by boiling the solution. It is also soluble in alcohol.

$\left\{ \begin{array}{l} 9.552 \text{ grains of chloride of platinum and petinine gave} \\ 5.930 \quad \dots \quad \text{carbonic acid, and} \\ 3.593 \quad \dots \quad \text{water.} \end{array} \right.$

By three determinations of platinum, the details of which have been already given, the mean per-centage of platinum was found to be  $\approx 35.46$ .

These results correspond with the formula  $C_8 H_{11} N, H Cl, Pt Cl_2$ .

Experiment.		Calculation.	
Carbon, . . . .	16.93	17.26	$C_8$ 600.0
Hydrogen, . . . .	4.17	3.96	$H_{11}$ 137.5
Nitrogen, . . . .	...	5.04	N 175.0
Chlorine, . . . .	...	38.29	$Cl_3$ 1330.4
Platinum, . . . .	35.46	35.45	Pt 1232.0
		100.0	3474.9

*Chloride of Mercury and Petinine.*—A solution of petinine in water, added to a solution of corrosive sublimate, gives a white precipitate, which dissolves in a considerable quantity of hot water, from which it is again deposited in crystals. It is much more soluble in alcohol; and the boiling solution gives a deposit of beautiful silvery plates on cooling. It is decomposed by boiling its watery solution, petinine being driven off, and a white powder deposited. It is readily soluble in the cold in dilute hydrochloric acid, probably with the formation of another double salt.

#### *Products of Decomposition of Petinine.*

The want of substance, which prevented the full investigation of the salts, has likewise curtailed this branch of the subject to a very few observations, which is the more to be regretted, as the general properties and low atomic weight of petinine give promise of definite products, which might enable us fully to determine its position in the chemical system.

When treated with concentrated nitric acid, it dissolves without any remarkable phenomena, and, on boiling, a feeble evolution of nitrous fumes takes place; but the petinine is attacked only to a very small extent, for, after being kept boiling for a long time, and then supersaturated with potass, it evolved the smell of the base apparently unchanged. Solution of chloride of lime immediately acts upon it in the cold, and develops a highly irritating odour, and some compound is manifestly produced; the solution remains colourless. Bromine water dropped into an aqueous solution of petinine occasions the precipitation of a yellow oil



heavier than water, and insoluble in acids,—the solution contained hydrobromate of petinine. From the analogy of the other volatile bases, we should expect this to be tribromopetinine,  $C_8H_7Br_3N$ . My material being exhausted, I was not able to extend these observations further.

*Picoline.*

Having determined the properties of petinine, I next turned my attention to that portion of the mixed bases which boiled between  $270^\circ$  and  $280^\circ$ , where I had every reason to expect the presence of picoline. After several rectifications, in each of which the first and last portions of the product were separated, I obtained a fine colourless transparent oil, possessed of all the properties of that substance. It dissolved readily in water: gave, with chloride of gold, a fine yellow compound depositing in needles from the hot solution, and with bichloride of platinum, a salt crystallizing in orange-yellow needles, analogous in all its properties to that of picoline. This identity was confirmed by analysis, which gave the following results:

$\left\{ \begin{array}{l} 5.648 \text{ grains of picoline from bone-oil gave} \\ 15.990 \quad \dots \quad \text{carbonic acid, and} \\ 3.998 \quad \dots \quad \text{water.} \end{array} \right.$					
Carbon, . . . .	77.21	77.41	$C_{12}$	900.0	
Hydrogen, . . . .	7.86	7.53	$H_7$	87.5	
Nitrogen, . . . .	14.93	15.06	N	175.0	
	<hr/> 100.00	<hr/> 100.00		<hr/> 1162.5	

For still further security, a determination of the platinum in its double salt with the chloride was made:

$\left\{ \begin{array}{l} 12.784 \text{ grains of chloride of platinum and picoline gave} \\ 4.204 \quad \dots \quad \text{platinum.} \end{array} \right.$	
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This corresponds to 32.88 per cent., and the calculation gives 32.94.

The suspicion, then, of the occurrence of picoline in the odore of UNVERDORBEN turns out to be perfectly correct; at the same time my experiments have clearly shewn, that odorene is a mixture of picoline, with at least one other base, the properties of which will be detailed in the second part of this investigation. The quantity of picoline contained in bone-oil is considerable, and it can be more readily prepared from that substance than from coal-tar naphtha; in fact, I obtained from three hundred pounds of bone-oil a larger quantity of picoline than that employed in my examination of it, which was obtained from some hundred gallons of coal-tar naphtha; and by means of it, I shall be enabled to trace out the products of its decomposition, which I was unable to pursue in my former communication



The presence of aniline in bone-oil I have already alluded to, and its quantity, though small, is by no means inconsiderable, when compared with that of the other bases. I did not think it necessary to take any further means for its identification than its highly characteristic reactions with chloride of lime and nitric acid.

The investigation of the other bases is not yet in a sufficiently advanced state for publication. The sparingly soluble one has been especially troublesome, and its purification is attended by difficulties which I have not yet fully overcome. The consideration of these will be taken up in the second part of this investigation.



XXXIII.—*On the Action of the Dry Gases on Organic Colouring Matters, and its relation to the Theory of Bleaching.* By GEORGE WILSON, M.D., Lecturer on Chemistry, Edinburgh.

(Read, April 17, 1848.)

#### I. Preliminary Remarks.

The remarkable power which chlorine possesses, of destroying all colours of organic origin, has long been an object alike of speculative and practical interest. The theory of bleaching, however, has hitherto remained imperfect, in consequence chiefly of the observation of Sir H. DAVY, that chlorine loses the power of decolorising when deprived of water. So striking is the difference, in this respect, between wet and dry chlorine, that it led the distinguished chemist mentioned, to deny to this gas the character of being essentially, or *per se*, a bleacher. He regarded as the true decolorising agent the oxygen of the water, which must be associated with chlorine before the latter can bleach. The late Dr TURNER has stated DAVY's view so shortly and clearly, that I quote his abstract in preference to any statement of my own. "DAVY," says he, "proved that chlorine cannot bleach, unless water is present. Thus dry litmus suffers no change in dry chlorine; when water is admitted the colour speedily disappears. It is well known also, that hydrochloric acid is always generated when chlorine bleaches. From these facts, it is inferred that water is decomposed during the process; that its hydrogen unites with the chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen, and of chromic and permanganic acids, of which oxygen is certainly the decolorising principle, leaves little doubt of the accuracy of the foregoing explanation."\*

The opinions of chemists on this point have now entirely changed. Chlorine is reinstated in the place it formerly held as the possessor of positive and intrinsic bleaching powers, and is looked upon as exerting these even when water is present. I quote Sir ROBERT KANE's views on this subject, as more fully expressed than the statements of most of our chemical authorities, and because he has demonstrated experimentally the falsity of DAVY's conclusion. "The theory," says he, in allusion to bleaching, "of this action of chlorine, which had been formerly thought to depend upon a mere oxidation of the colouring matter, water being decomposed, has been shewn by my results with orceine, and confirmed by those of ERDMAN on indigo, to consist in the formation of new substances con-

\* Elements of Chemistry, 7th edit., p. 275.



taining chlorine. The chlorine in some cases replaces hydrogen; in others, it combines directly with the colouring matter; in others, again, water is decomposed, and the product, besides containing chlorine, is also more highly oxidised.\*

Beautiful, however, and satisfactory as the investigations of KANE, ERDMAN, DUMAS, LAURENT, and others are, they leave unconsidered the question, why has chlorine, which so rapidly and permanently destroys the colour of organic compounds when moist, no action on them when dry?

The object of the researches I am about to detail, is to supply, in part at least, this defect in the theory of bleaching, by endeavouring to shew how the removal of water from chlorine arrests or suspends its decolorising power. Before entering at length into this question, however, I would observe, that DAVY's conclusion, that oxygen is the efficacious bleaching constituent of moist chlorine, cannot be regarded as marked by the felicity which generally characterised that great chemist's interpretations of obscure or complicated phenomena.

1. His view assumed, against all probability, that the acknowledged great affinity of chlorine for hydrogen would be exerted solely towards the hydrogen of water, but not towards that present in a colouring matter; or at all events, that the affinity in question would be efficacious only in relation to the elements of water. We certainly must set aside, as entirely arbitrary, the notion, if that were implied in DAVY's statement, that chlorine in the presence of two bodies—water and a colouring matter—each containing hydrogen, would be indifferent to that element, as a constituent of the one, but eager to unite with it as present in the other. Although free chlorine, however, must be regarded as equally ready to unite with the hydrogen of every compound which comes within the sphere of its affinity, it does not follow that it will obtain that element with equal ease from every substance containing it. On the other hand, we may be certain, that those more unstable compounds which part most readily with their elements, will be the first to have the hydrogen removed from them by chlorine, whilst less easily decomposed substances may resist its action altogether. DAVY's view, however, gains nothing from this acknowledgment; for it represents water, an enduring compound of but single equivalents of two elements, as compelled to abandon its hydrogen to chlorine, whilst the proverbially fading colouring principle of a flower or an insect—a frail combination of many equivalents of three or more elements—is assumed to be able to retain its hydrogen unaffected by chlorine. In the justice of such a conclusion, no chemist could concur.

2. Again, DAVY's argument proved too much, and was in truth, self-destructive; for if chlorine be denied the character of a positive bleaching agent, because it does not bleach when dry, then oxygen, judged by the same rule, must

\* Elements of Chemistry, p. 1054.



be refused that character also, for when the latter gas is deprived of moisture, it is more indifferent to colouring matter than even chlorine. DAVY's reasoning, then, if pushed to its logical consequences, conducts us to the strange conclusion that since, when moist chlorine bleaches, the chlorine and oxygen are not the active agents, and the only other body present except the colouring matter is hydrogen, which certainly does not decolorise when dry, bleaching must be regarded as an inexplicable phenomenon, an effect without a cause.

It would not be difficult to point out other objections to the consistency of DAVY's opinion; but those given may suffice to prove that, before the analysis of the products of chlorine-bleaching shewed the erroneousness of his conclusion, its inherent untenableness admitted of easy illustration.

## II. *Influence of Sunlight on the Bleaching Action of Dry Chlorine.*

The chief object of the experiments which this paper details was, to ascertain the cause of the indifference of chlorine when free from moisture to anhydrous organic colouring matters. But before entering on this inquiry, it occurred to me to doubt, whether DAVY's original proposition, that dry chlorine does not bleach dry colours (which seems to have been universally assented to by his successors), could be admitted without limitation.

A repetition of his experiments appears, at first sight, to justify unconditionally his conclusion. Among the specimens which accompany this communication are two sealed tubes, containing blue and red litmus-paper shut up in an atmosphere of chlorine. The paper was first dried in a current of air previously passed through chloride of calcium. A stream of carefully desiccated chlorine was then sent over the paper for five minutes, and the tube, whilst full of gas, sealed at the blow-pipe. The coloured papers were thus exposed, in the first place, to the bleaching action of some sixty cubic inches of chlorine; and have, in addition, remained in contact with that gas since the 28th of July 1847, a period of more than eight months, yet they still retain their original tints, though somewhat faded. Had water been present in these experiments, the colours would have been irrecoverably destroyed in a few seconds, or minutes at the farthest.

Striking as these results are in supplying confirmation of DAVY's views, they are curiously contradicted, or rather qualified, by other experiments, differing from those just mentioned, as to mode of trial, only in one particular.

The affinity of chlorine for hydrogen, when both gases are free, is greatly modified by the action of sunlight, so that whilst in perfect darkness they may be kept mingled without combining, they unite with explosion if exposed to the direct rays of the sun, and more or less rapidly in diffuse daylight, according to its intensity. So faithfully, indeed, do free chlorine and hydrogen obey what natural



philosophers and chemists have agreed to call the actinic influence of the sun-beam, that the mixed gases contained in a graduated tube over water are found to form a delicate actinometer, the intensity of the actinism being measured by the rapidity with which the water rises in the tube, as it dissolves the hydrochloric acid produced by the union of the gases.\* This actinic exaltation of affinity, so striking when both gases are free, continues to manifest itself, though less powerfully, when chlorine is in contact with substances containing hydrogen, although the latter is in a state of combination.

Chlorine water remains unchanged in the dark, but is rapidly converted by sunlight into hydrochloric acid, and free oxygen. Dutch liquid, chloroform, and chloric ether, besides various other bodies, are known to give up their hydrogen to chlorine much more swiftly when exposed to the direct rays of the sun than if shaded from them. It seemed in the highest degree probable that the hydrogen of organic colouring matters would, in like manner, resist the action of dry chlorine for a much shorter period in sunlight than in diffuse daylight, or in darkness. To determine this point, the following experiment was tried. A wide glass-tube, open at both ends, was constricted in the middle so as to present a narrow central canal, like that of an hour-glass. Pieces of blue and of red litmus-paper were then placed on either side of the constricted portion, and the open ends of the tube drawn out at the blow-pipe, so as to admit of their being put in communication, by means of caoutchouc connectors, with an arrangement for drying the paper, and furnishing chlorine. After the paper had been exposed to a current of dried air at the temperature of 220° Fahr. for three hours, washed chlorine, transmitted through Nordhausen sulphuric acid, and a tube three feet long containing fused chloride of calcium, was sent along the double tube containing the papers, for five minutes. The ends of the tube were then sealed whilst it remained full of gas, and the constricted middle portion closed and divided at the blow-pipe, so that the double tube was converted into two single hermetically sealed ones, each containing dried litmus-paper in an atmosphere of chlorine. In this way two tubes were procured, each containing portions of the same coloured paper, which had been dried in the same current of air, and exposed in exactly similar circumstances to the same stream and the same amount of dry chlorine.

The one of these twin tubes was hung up inside a window, with a western exposure, on or about the 31st of July 1847. The other was laid aside in a cupboard, out of reach of the direct rays of the sun, but not protected from the influence of dull daylight. It was frequently brought out, moreover, to be examined, and was at no time during the day in absolute darkness. I shew the Society this tube after remaining in the circumstances described for more than eight

\* Lond. and Edin. Phil. Mag., 1844, vol. xxv., pp. 2-3.



months. The inclosed papers still retain their original colours little altered; and in perfect darkness would, in all probability, have retained them still better. Side by side with this tube I have placed its twin, which was exposed to full sunshine, and the papers in which are bleached to the purest white. In how short a time his change occurred I cannot precisely say, as absence from town between the 1st of August and the 16th of September 1847 prevented me from watching the progress of the actinic bleaching. But, on the last-mentioned date, I found the paper completely decolorised, so that six weeks of sunshine sufficed totally to bleach paper in dry chlorine, whilst that gas excluded from direct sunlight has failed to produce the same effect in eight months and a half.\* In another quite similar experiment, the results were much less striking. A tube with dry chlorine and litmus-paper has hung since 1st August 1847 in a western exposure, yet, at the date of my writing, (April 13, 1848), the litmus-paper, though much faded, as appears when it is contrasted with the contents of the twin tube which was kept out of sunshine, is far from being entirely bleached. This difference in result leads to the suspicion, that in the experiment first recorded, the chlorine or the paper may not have been so dry as both were in the second trial. Great precautions (the same in both cases) were taken to secure absence of moisture from the gas and the paper, but I know of no test of perfect dryness applicable to gases, and I cannot affirm that, in either case, the chlorine or the colouring matter was absolutely anhydrous. Nor does it admit of doubt that the presence of even a trace of water would sensibly quicken bleaching under sunlight, which rapidly decomposes chlorine-water. Yet every chemist will acknowledge that chlorine, which could be retained over litmus without bleaching it for nearly nine months, must have made a close approximation to perfect dryness. We are as yet, moreover, too ignorant of the laws and conditions of actinic action, to know well how to dispose of apparent discrepancies in its effects.

I could not try more than the two experiments recorded, last summer, and I did not think it desirable to attempt a repetition of them during the clouded season of the year. Meanwhile, different as is the testimony these experiments afford, as to the rapidity of actinic chlorine-bleaching, they agree in proving that darkness, as well as dryness, is essential to the preservation of organic colours from destruction by chlorine, and that this gas, at least when assisted by sunlight, is a positive bleacher. DAVY's original proposition must be accepted with this qualification.

I close my remarks on this subject, with the observation, that in bleaching on the large scale it should make a sensible difference on the rapidity of the process, whether it be carried on in open sunlight, or in exclusion from it. Our present bleaching process is as rapid as could well be wished, so that it is not in the direc-

\* The papers shut up with chlorine, and kept in darkness, have not become bleached by two months' longer retention in the gas June 19, 1848



tion of quickening his methods, that the practical bleacher probably desires improvement. One may expect, however, that the same amount of chlorine, especially if moist, should be more efficacious in bleaching, if assisted by sunlight, than if debarred from it; or what comes to the same thing, that a small amount of chlorine should, in practice on the great scale, bleach as powerfully in sunshine, as a larger one in darkness. It might be possible, accordingly, to economise chlorine, or chloride of lime, in this country, in the brighter seasons of the year, and at all times in sunny climates, if the bleaching operations were carried on in the open air.

### III. *Influence of Water over the Bleaching Action of Oxygen, Sulphurous Acid, and Sulphuretted Hydrogen.*

The fact that actinised chlorine bleaches, though dry, supplies no explanation of the function which water performs, when it invests that gas with decolorising power. With a view to solve this problem, I made two series of experiments; 1st, The object of the one was to observe to what extent other bleaching gases resemble chlorine in being dependent for bleaching power on the presence of water, and likewise to ascertain whether the acid gases and the volatile alkali, when made anhydrous, lose that power of changing the tints of dry organic colouring matters, which characterises them when moist. These experiments promised to shew whether the action of dry chlorine on colours is exceptional and anomalous, so as to demand a special explanation, such as DAVY gave, or but a particular case of a general law, to which all elastic fluids are obedient.

2d, The object of the other set of trials was to determine, whether bleaching power can be conferred upon dry chlorine, by dissolving it and anhydrous colouring matters in liquids containing no oxygen. I begin with the experiments first referred to.

Five gases besides chlorine have marked bleaching powers when in the condition of perfect elastic fluidity, and not anhydrous, viz., chlorous acid, hypochlorous acid, sulphurous acid, sulphuretted hydrogen, and oxygen.\* To these may be added provisionally, the curious body *ozone*, which BERZELIUS regards as an allotropic form of oxygen, and SCHOENBEIN as a volatile peroxide of hydrogen. I have made no experiments with this substance, because, in the present state of our knowledge concerning it, it could not supply crucial results. Chlorous acid is too explosive to admit of satisfactory researches being made with it. The same remark applies with limitation to hypochlorous acid, a substance so interesting, from its high bleaching power, and its containing, like chlorous acid, the two most important bleaching agents, chlorine and oxygen. I have made no experiments with this substance, but PELOUZE has quite recently supplied us with a new and much

\* I omit from this list hydrogen, because, although it bleaches powerfully in the nascent state, it has no sensible bleaching action, whether moist or dry, after it has attained the condition of perfect gaseity.



more manageable process for preparing it, by means of which we may hope to make researches as to its action on colours.\* My experiments have been limited to sulphurous acid, sulphuretted hydrogen, and oxygen. I begin with the last as the chief rival in bleaching power of chlorine.

*Oxygen.*

I have not thought it necessary to make many experiments with oxygen, as to its relative bleaching power when moist and dry. Test papers can be preserved for years, without sensibly changing tint in air, *i. e.*, diluted oxygen, only moderately dry, especially if free exposure to light be avoided. The general experience of mankind has led to the same conclusion, in reference to the comparative permanence of tint, of dyed tissues kept in the shade. I have exposed coloured papers for four and five hours to a current of dry air, without permanently altering their hue. The paper in such trials always exhibits a duller tint at the end than at the beginning of the experiment; but that this is the result merely of its loss of water, is evident from the fact that, on moistening the paper, the original brightness of tint is restored. No one, probably, will dispute the conclusion, that dry oxygen does not, at least in darkness, bleach more than dry chlorine.

The effect, on the other hand, of the addition of water to oxygen in increasing its decolorising power, is so strikingly demonstrated by the practical experience of the domestic bleacher, that experiments on the small scale did not seem necessary to prove the fact. No point is more attended to, in the familiar practice of bleaching cloth by free exposure to rain, wind, and sun, than the constant keeping of the tissue wet. I am far from affirming that other important agencies, such as the actinic, concerned in the bleaching, are not affected by the presence of water; yet I think no one will doubt, that one important function it serves, is the increasing (I do not at present say how) the bleaching action of the oxygen of the atmosphere.

The unquestionable decolorising power of peroxide of hydrogen, chromic, and permanganic acids, to which Dr TURNER refers as confirming DAVY'S view regarding the bleaching action of moist chlorine, only demonstrates that *nascent* oxygen bleaches, and is of no service in proving that that gas, when in its state of perfect elastic fluidity, possesses bleaching powers. The nascent hydrogen of decomposing water bleaches readily; so that, if Dr TURNER'S view were accepted as valid in relation to oxygen, a theory of chlorine-bleaching might, with some plausibility, be defended, in which hydrogen, instead of, or as well as, oxygen, should be represented as the positive bleaching agent in chlorine-water.

\* It would be peculiarly interesting to observe the effect of drying this gas in modifying its action on colouring matters. Should it lose its bleaching power when dry, it would be curious to watch the effect of exploding it in the presence of an anhydrous colouring matter. The result would shew whether *nascent* oxygen and chlorine bleach as powerfully when *dry* as moist.



*Sulphurous Acid.*

The bleaching power of moist sulphurous acid is so well known, and has so long been turned to account in the arts, that I need enter into no details in proof of the gas possessing this property. With a view to determine whether it loses its bleaching power when made anhydrous, I passed washed sulphurous acid, obtained by the action of mercury on oil of vitriol, through strong sulphuric acid, and over chloride of calcium, so as to deprive it of moisture. The gas was then made to stream for five minutes through a tube containing blue litmus-paper, carefully dried, and the tube hermetically sealed while full of the gas. This experiment was made on March 31, 1848. The paper was not altered in tint during the passage of the gas, and at the present date (April 17) it remains unchanged.\* I made a similar experiment on the 10th of July 1847, only the sulphurous acid, being obtained by the action of charcoal on oil of vitriol, was mingled with carbonic acid. The mixed gases were passed dry over blue litmus-paper for seven minutes, but did not change its tint in the slightest; the tube was then sealed, and is included among the specimens laid before the Society. After the lapse of nearly nine months, the paper continues not appreciably altered. Gaseous sulphurous acid, then, is no better bleacher when dry than chlorine.

*Sulphuretted Hydrogen.*

The other remarkable properties of sulphuretted hydrogen have prevented its bleaching power from attracting very much attention; nevertheless, it has long been recognised. Nascent sulphuretted hydrogen bleaches powerfully. An acidulated infusion of litmus has its colour rapidly destroyed by the addition to it of a metallic sulphuret, such as that of calcium, barium, or iron. The free gas bleaches much less distinctly, yet its action is tolerably rapid. In proof of this, I have sent with this communication a tube, which, after the blue litmus-paper contained in it had been dried, was opened for a few seconds to the atmosphere, in consequence of a derangement of the apparatus. The paper was thus exposed for a very short period to the amount of vapour which is diffused through air at the temperature of about 60° F. Immediately after this accident, carefully-dried sulphuretted hydrogen was passed over the litmus for five minutes, and the tube sealed. The paper was distinctly, though faintly, reddened during the passage of the gas, and after the lapse of about twenty hours the colour was found almost completely gone. In contrast with this result obtained with slightly moist sulphuretted hydrogen, I shew the Society a tube containing dry blue litmus-paper, and brown-red rhubarb paper, which were exposed to the action of equally dry sulphuretted hydrogen for six minutes. The papers were not altered in tint.

\* The colours are still unaltered; a remark which applies also to the experiment next recorded, June 19, 1848.



They have remained sealed up in the tube, in an atmosphere of the gas in question, since July 9, 1847, when the experiment was made. No decided change was observed in the tints of the papers up to July 30, when I ceased to make notes of their appearance. The rhubarb paper is now little altered, but the blue has, here and there, a few small red spots, some with white borders upon them. Both tints, however, are still, after so many months' exposure to the gas, very slightly affected.\* I shew the Society also tubes containing blue paper, which were exposed for five minutes to dry sulphuretted hydrogen on the 25th March 1848, and have since remained shut up in the gas. They exhibit, at the present date (April 17), no sensible change in tint.† Sulphuretted hydrogen, then, has its bleaching power arrested by depriving it of water.

#### IV. *Action of the Acid Gases and of Ammonia on Organic Colours.*

I pass now to the acid gases and ammonia, which so characteristically alter the tints of organic colouring matters, when water is present. The gases I tried were, sulphurous acid, carbonic acid, sulphuretted hydrogen, and hydrochloric acid, in addition to the volatile alkali.

##### *Sulphurous Acid.*

I need not say anything further concerning sulphurous acid, as it is implied in what was stated as to its negative action on vegetable blues, that its reddening action is as much arrested as its bleaching one by depriving it of water. Dry sulphurous acid, I also find, does not change alkalised turmeric or rhubarb paper to yellow.

##### *Carbonic Acid.*

I have already referred to the retention of its full blue tint, by dry litmus-paper, exposed for many months to a mixture of anhydrous carbonic and sul-

\* The papers have not sensibly altered after the lapse of two additional months; nor is there any change in the litmus-paper referred to in the next experiment, June 19, 1848.

† One of the arguments in favour of the "Binary Theory of Salts" is the fact, that the so-called oxygen acids do not affect vegetable colours unless associated with water, which they are assumed to decompose, so as to become by appropriation of its elements hydracids of new radicals. The experiments recorded in the text, however, shew that one hydracid, at least, has its action on colouring matter as much negated by the withdrawal of water as any oxyacid. It does not follow that the rationale of the change is the same in both cases; but the fact that anhydrous gaseous hydrosulphuric acid does not redden vegetable blues, lessens the value of the argument alluded to. In the great majority of cases, the rendering of an oxyacid anhydrous implies its alteration from the liquid state to the solid or gaseous one. This change in condition is of itself sufficient to alter most materially the influence of a reagent. It appears, however, to have been altogether overlooked in explaining the indifference of a dry oxyacid to organic colours. The phenomena recorded further on, as observed with gaseous hydrochloric acid and liquefied sulphurous acid, bear upon this point, but it cannot be discussed at length here.



phurous acid gases. Pure carbonic acid is equally negative in its action on vegetable blues and browns.

*Sulphuretted Hydrogen.*

Sulphuretted hydrogen, even when moist, does not change organic colours to so great an extent as the stronger acids do. Solutions of litmus, *ex. gr.*, become, under its action, only of a purple-red tint, like that which carbonic and boracic acids give them, whilst the more powerful acids destroy all shade of blue. If I may judge from the few experiments I have made on this subject, the reddening power of sulphuretted hydrogen is more dependent than its bleaching action on the presence of water. At all events, it is equally dependent on moisture, for blue litmus has been reddened very slightly by eight months' exposure to the dry gas, neither has brown rhubarb paper become yellow, or appreciably grown paler.

*Hydrochloric Acid.*

No acid excels hydrochloric in full and rapid action on organic colours; nor is any one, according to the prevailing opinions of chemists, less likely to be indebted to association with water for its characteristic properties. It is the simplest type of a perfect acid, and as such, might be expected to exhibit, even when gaseous and anhydrous, the same relation to organic colours which it does when moist. I looked upon hydrochloric acid, therefore, as the most interesting of the acid gases with which experiments could be made.

I have not hitherto referred particularly to the method followed for drying the gases, because none of those I have yet mentioned present great difficulties in the way of rendering them,—I will not say certainly anhydrous,—but at least sufficiently dry not to affect colours. It is otherwise with hydrochloric acid. I have failed more frequently than I have succeeded, in rendering this gas, by drying, indifferent to colours; nor have I been able to preserve blue litmus for any length of time unchanged in an atmosphere of the dry gas. It is necessary, therefore, to be more particular in describing the process for drying, which was followed with hydrochloric acid; although it differed in no respect from that pursued with the majority of the other gases.

The general arrangement, especially in the later and more perfect trials, was the following:—The thinnest India letter-paper was stained with an infusion or tincture of the colouring matter intended to be used, and afterwards dried at the temperature of the air. Slips of the paper were introduced into a tube, varying in different cases from half an inch to one inch in diameter, and from six to eighteen inches in length. The tube was then hermetically sealed at one extremity, and drawn out at the other into a narrow canal, which was left open. A



smaller open tube was afterwards attached to each side of the larger one, near to its shut end, so as to communicate with its cavity. These lateral tubes projected for a short distance at right angles to the long axis of the larger tube, and then ran parallel to it, with their open mouths pointing in the opposite direction from that of the single canal at the other end of the tube. To prevent confusion, I shall call the lateral appendages which I have described, the horns of the tube.

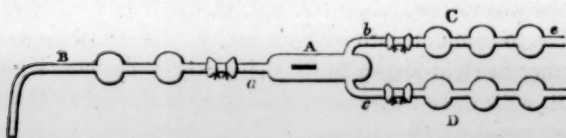
When the latter was arranged for an experiment, the narrowed termination at one end was placed in communication with a short tube filled with chloride of calcium, by means of a caoutchouc connector. The free extremity of this tube was bent at right angles, and dipped into oil, so as to cut off communication with the outer air. To each of the open horns, also, a chloride of calcium tube, three feet in length, was attached. The one of these tubes was intended to convey, and render anhydrous, a current of air, which should dry the paper. The other, in like manner, was to carry and dry the gas, which should be brought in contact with the paper, when the latter was deprived of moisture. At the beginning of an experiment, the tube through which the gas subsequently passed, after being connected with one of the horns, was sealed at the end furthest from the paper. Its presence from the first was essential, because otherwise the dried paper must have been put in communication with the moist outer air, when a fresh chloride of calcium tube to carry the gas was substituted for that which previously conveyed the air: for if the same tube in whole, or in part, had been employed, first to dry the air, and then the gas, the freedom of the latter from moisture could not have been counted upon.

I found, after trying various devices, a pair of common bellows the most convenient instrument for furnishing a current of air. The air was first passed through a bulbed tube, immersed in a freezing mixture, and then through the chloride of calcium tube into the one containing the paper; from which it escaped through the smaller drying tube that dipped into oil, as already mentioned. The paper was maintained by gas lights at a temperature of about 220° Fahr., and the air was kept passing over it, for at least two, generally for three, hours.

When the paper appeared perfectly free from moisture, the lateral horn, by which the air reached it, was sealed at the blow-pipe, and the drying apparatus detached. The shut end of the other long chloride of calcium tube was then opened, and connected with an apparatus for furnishing the gas to be used in the experiment.

The woodcut on the following page will make the description more intelligible. Only the more essential parts of the arrangement are represented in the diagram; the bellows and connecting flexible tube on the one hand, and the retort in which the gas was generated on the other, as well as the washing bottles, &c., being omitted.





A, Tube in which coloured paper was placed.

a, Narrow canal, communicating by a caoutchouc collar, with small tube containing chloride of calcium.

b and c, Lateral appendages or horns, communicating with long drying tubes, C and D.

B, Small drying tube, dipping into oil, through which the elastic fluids, after passing over the paper, escaped into the air.

C, Long drying tube, which was sealed at e, at the commencement of an experiment, but opened when the paper had been dried, and employed to convey the gas which was to act on it.

D, Second long drying tube employed to carry air, to render the paper in A anhydrous. When the paper was dried, the horn c was sealed at the blow-pipe, and D detached. Gas was then transmitted through C.

The arrangement I have described was followed with all the gases except ammonia. Chlorine and sulphurous acid were sent through oil of vitriol before reaching the chloride of calcium tube. The other gases were generally passed simply through a bulb immersed in a freezing mixture, before being transmitted through the drying tube. I found it essential to success in the experiments recorded to dispense with corks, asbestos, and cotton, in connecting or loosely stopping the tubes, as these bodies retained moisture with the greatest obstinacy. Caoutchouc collars were used in every case to unite the detached portions of the apparatus. The special devices followed in particular cases are mentioned under the gases which called for them.

I procured hydrochloric acid gas by the action of Nordhausen sulphuric acid on common salt previously fused. Theoretically, the gas should carry with it a mere trace of moisture, yet in spite of the apparently effectual drying apparatus made use of, the acid, in the majority of trials, changed the tint of blue litmus as soon as it came in contact with it, giving it a dark lilac or deep wine-red colour. Nevertheless, on three occasions I was able to pass a current of dried hydrochloric acid for five minutes over blue litmus-paper, without sensibly altering its tint, according to the judgment of four persons besides myself, who were witnesses of the experiments. These positive results outweigh the negative ones already referred to. The majority of the latter, moreover, were only partial failures, and went the length, at least, of proving that the removal of moisture from hydrochloric acid gas delays, if it does not prevent, its characteristic action on organic colours. In the successful experiments mentioned above, the negative action of the acid was only transient; for when the tubes containing the gas and paper were sealed and set aside, the colour invariably passed from its original blue tint to a more or less decided red. In several trials, however, the ultimate effect of the hydrochloric acid fell far short of the full reddening which



even the slightly moist gas produces. I shew the Society a tube, containing litmus-paper, which withstood, without change, a current of hydrochloric acid passed over it for five minutes. The experiment was made on 23d February 1848; and the paper is at this date not a bright red, but only a dark lilac.

Three explanations suggest themselves as to the ultimate though imperfect reddening of the blue litmus. 1. The gas may not have been quite dry. 2. Hydrogen acids, though perfectly dry, may, unlike the so-called oxygen acids, be able to modify the tints of colours. 3. Hydrochloric acid, which has a great affinity for water, can compel its elements to unite to form it, so that the gas may combine with the liquid. Hydrogen and oxygen are present, both in the colouring matter and in the paper. In the paper, indeed, they are present in the proportion to form water. This solvent, therefore, may be slowly generated within the sealed tube, and be the cause of the gradual reddening of the blue paper.

As to the first of these views, I can neither disprove nor confirm it. It is probably as difficult to render a gas absolutely anhydrous, as it is to produce a perfect vacuum. Moreover, as I have stated already, we have no test of absolute dryness, applicable to a gas. It would interrupt the argument, however, to consider this question at length here; I have devoted, accordingly, the section which succeeds this to its discussion.

Of the second explanation, I would say much the same as I have said of the first. It is highly probable that a powerful hydracid like the hydrochloric should retain, more or less, as a gas, its characteristic action on organic colours.

I would speak most positively of the third view. The power of bodies which have a great affinity for water, to compel its formation and separation, is so great, that I ventured to predict, that it would be impossible to preserve, for any length of time, blue litmus unchanged in tint in the driest hydrochloric acid. I do not dwell at length, however, on the cause of the ultimate reddening, as the fact that the paper was only slowly and imperfectly reddened, is sufficient for my present purpose. At lowest, the experiments I have detailed demonstrate that the removal of water from hydrochloric acid gas delays its action on colours.

#### *Ammonia.*

The last of the gases I tried was ammonia. According to KANE,\* when dry it has no action on organic colours, although no body, when moist, affects these substances more powerfully. I might content myself with adducing this distinguished chemist's statement as to the negative action of dry ammonia, and add it to the list of gases which have their action on colouring matter arrested by the removal of moisture. My own experiments, however, have been so much less decisive than KANE's statement led me to expect they would be, that I cannot, without comment, avail myself of his evidence. The difference between his results and

\* Elements of Chemistry, p. 852.



mine is probably sufficiently accounted for by the supposition, that I did not thoroughly dry the ammonia. This gas is more difficult to render anhydrous than even hydrochloric acid; not so much, perhaps, because it has a greater affinity for water, but because our most powerful desiccating agents, such as the deliquescent chlorides and oil of vitriol, cannot be employed to dry it. We are restricted, accordingly, to substances much less hygrometric, such as unslaked lime, hydrate of potass, and its fused carbonate.

It would serve no purpose to record a series of unsuccessful experiments: I merely mention, therefore, that I have never been able to obtain ammonia in a condition in which it did not change the tint of reddened litmus and of yellow turmeric paper as soon as it came in contact with them. I have found its action on colouring matter, however, sensibly reduced by passing it over the hygrometrics last referred to. Reddened litmus, for example, became only purple when it first encountered dried ammonia, and did not acquire a bright-blue tint, when left in the gas, till after the lapse of some hours.\* For the reasons mentioned above, I do not, in the meanwhile, feel myself at liberty to say more than that the presence of water greatly quickens the action of ammonia on colours.

It would appear, then, from the results I have detailed, that there is little, if anything, anomalous or exceptional in the negative bleaching of dry chlorine. Oxygen, sulphurous acid, and sulphuretted hydrogen, are equally powerless as bleachers, when deprived of moisture, as that gas. Sulphurous and carbonic acids are probably more indebted than chlorine to water for their power of modifying colouring matters, both as regards changing and destroying their tints. Hydrochloric acid and ammonia have their influence on colours at least temporarily arrested by the absence of water; and, after all, it is a question with the whole of the gases referred to, only of degree. It is not likely that even in absolute darkness chlorine has no action on anhydrous colouring matter. If this be conceded, the whole of the gases referred to may be included in one category, as having their modifying action on organic colours accelerated by the presence and retarded by the absence of water. I trust to supply an additional datum towards the settlement of this question, by observing the difference which exposure to sunlight makes, in relation to the action of all the gases with which experiments were tried.

\* In the experiment which yielded the most successful result, the ammonia was first passed through a bulb immersed in a freezing mixture, and afterwards through long tubes containing lime, caustic potass, and its fused carbonate. The gas was then allowed to flow through a tube for some minutes till it had expelled the air, and the tube was sealed. The one end of this tube had been previously expanded into a large ball, which was filled with fragments of the hygrometrics just mentioned: in the other end of the tube a small sealed bulb was placed, containing a piece of carefully dried red litmus-paper. The ammonia was left in contact with the drying agents for a week, when the tube was shaken till the bulb broke, and allowed the gas and the paper to meet. The latter, as mentioned in the text, immediately became purple, and after some hours bright blue.



Before proceeding to detail the second series of researches, I have thought it desirable to offer some observations on the processes employed for drying gases.

V. *On the Methods applicable to the Drying of Gases.*

The methods at present in use for drying gases cannot be considered as yielding more than an approximation to absolute dryness in the case of any elastic fluid. The processes employed are inherently defective, both mechanically and chemically. When chloride of calcium and pumice-stone, steeped in oil of vitriol, are employed as the desiccating agents, they cannot be made use of except in fragments of considerable size, otherwise the containing tubes become choked, and the gas does not pass. Interstices, accordingly, comparatively speaking large, occur between the separate fragments of the drying agent; and the gas, in moving along, has a certain portion of its mass not in physical contact with the hygrometrics, or directly exposed to their desiccating action. In like manner, when a gas is sent through a column of oil of vitriol, only the surface of each bubble is in contact with the liquid, and the gas-bells rise very rapidly through so dense a fluid, so that they can be dried only imperfectly during their ascent.

Those defects admit only of partial remedy, by extending the surface of chloride of calcium or pumice-stone, or by multiplying the columns of oil of vitriol through which the gas shall pass. A practical limit is set to such devices by the obstruction which they offer to the passage of elastic fluids. This can be overcome only by increasing the pressure at which the gas is delivered, and it is not easy to regulate this, so that the gas shall not flow in too swift a current, and so neutralise, by the rapidity of its passage, the benefit which would otherwise result from its coming in contact with an extended hygrometric surface.

The imperfections just alluded to are not, perhaps, beyond the reach of suitable mechanical contrivances; but even if they were all remedied, the important question still remains, will the protracted and complete contact of a gas containing water-vapour with the most powerful hygrometrics, suffice entirely to deprive the gas of moisture? With a view to determine this point, I shut up muriatic acid gas, previously passed through a freezing mixture, and over chloride calcium, within a glass tube containing fragments of the same salt. It was left for a week in contact with the chloride, and then allowed to meet carefully dried blue litmus-paper, enclosed along with it at the commencement of the experiment, in a small sealed bulb of thin glass, which was readily broken by shaking the tube. The paper began to change tint as soon as it met the gas; and if this alteration in colour be accepted as an evidence of moisture being present in the muriatic acid, then the latter was not dry. A similar experiment, with a like result, has already been related in reference to ammonia.

These results, however, are not decisive of the point whether the gas was anhydrous or not, for the change in tint of the litmus may possibly be accounted



for otherwise than by assuming the presence of water; and the fault, moreover, even if water were present, may have lain with the coloured paper, not with the gas. The same objection does not apply to the following observation. If air at the temperature of  $60^{\circ}$  F. be sent through a long tube filled with fused chloride of calcium, it parts with moisture, which the chloride absorbs and combines with. If this dried air be thereafter transmitted over moist chloride of calcium, the latter becomes, to appearance, speedily dry. Here we have the apparently contradictory results of chloride of calcium drying air, and air drying chloride of calcium. The inference seems unavoidable, that there must be a neutral point where the chloride of calcium and air will be mutually indifferent, so that neither shall be able to deprive the other of moisture. This point will vary in reference to, 1. the relative quantities of the hygrometric salt and air acting on each other; 2. the relative dryness of the gas and solid; and, 3. the temperature at which the trial is conducted. Experiments on gases are generally made in apartments having an average temperature of or about  $60^{\circ}$  F., at which the tension of water-vapour is probably great enough to resist, so far as complete condensation is concerned, the absorbing power, and affinity for it, of all hygrometrics. This remark leads directly to the observation, that reduction of temperature is probably the most effectual of all processes for drying a gas. It has been employed with great success by FARADAY, in his later researches on the liquefaction of the gases;\* and I was induced, in consequence, to make use of it in my experiments. The value of the method admits of easy demonstration. The great obstacle to rendering a gas anhydrous, is the tension which heat confers on the water-vapour diffused through it. We generally endeavour to overcome this tension by opposing to it the condensing force of porous hygrometrics, and the chemical affinity of substances which combine readily with water; yet it is not at all certain that these forces have the maximum condensing power attributed to them. On the other hand, it is certain, that the tension of water-vapour is exceedingly small at zero, and rapidly decreases as we descend the thermometric scale.

FARADAY'S discovery, moreover, of the existence of a limit to vaporisation, teaches that there must be a temperature at which ice abruptly ceases to give off vapour. If this point be within reach of our frigorific appliances, and were ascertained, we should possess, in the reduction of gases to this temperature of no vapour, a theoretically perfect process for rendering gases anhydrous. It would be applicable, however, only to the less condensible elastic fluids, for the more easily liquefied ones would become liquid before the temperature of no-water vapour had been attained. It is further to be noticed, and the remark is important, that all volatile bodies have their vaporising point lowered in the presence of bodies more volatile than they are. The fact is familiar to every chemist. The

\* Phil. Trans., 1845. Part I., p. 155.



essential oils, *ex. gr.*, whose boiling points are much above that of water, are entirely dissipated in vapour if mingled with water raised only to the temperature of 212° F. Even bodies ranked, when anhydrous, among fixed substances, such as common salt, nitre, and boracic acid, rise with the vapour of water below its boiling point. It cannot be doubted that, in like manner, a temperature sufficiently low to hinder ice from volatilising *in vacuo*, or in still air, would not prevent it yielding a continuous stream of vapour in a current of gas. This power, indeed, of gases, as the more volatile bodies, to solicit and compel water-vapour to accompany them, is, at all temperatures, but especially at high ones, a formidable obstacle to rendering elastic fluids anhydrous. On the other hand, this diffusive power greatly increases the desiccating effect of gases, even not absolutely dry, when sent in currents over moist solids.

How near an approximation may be made to perfect dryness in the case of gases, cannot be determined till we have a test of the anhydrous state applicable to elastic fluids. A criterion of some value would be the passage of a considerable volume of the gas (ammonia excepted), through a weighed tube containing chloride of calcium, which should not increase in weight if the gas were anhydrous; but, if the preceding observations are well founded, this test would cease to act before the gas was quite dry.

I have tried whether the change of tint which the so-called sympathetic inks (solutions of the salts of cobalt and nickel) undergo when deprived of water, would serve as an indication of dryness on the part of gases; but I find that it is a test of no delicacy.

Indifference to colouring matter will certainly be found a negative indication of some value. Chlorine, *ex. gr.*, which immediately bleaches, and sulphurous or carbonic acid, which reddens litmus, cannot be dry. This test, of necessity, is limited to the gases which affect organic colours, and would be useless in the case of oxygen, nitrogen, hydrogen, the carburetted hydrogens, &c. &c.

A convenient way of examining the dryness of gases by means of colouring matters is to prepare, by blowing at short distances along a thin glass-tube, a series of small bulbs, in each of which a piece of litmus-paper may be placed. The papers are then to be dried in a current of air, passed through oil of vitriol and over chloride of calcium, and each bulb sealed off separately. In this way, a large number of bulbs can be prepared at the same time, and kept ready for use when required. One of these is to be placed in a tube forming part of the arrangement employed in the particular experiment, so that it shall be enveloped in the gas whose dryness is to be tested. By a sharp tap on the tube, the enclosed bulb is easily broken, and the gas and paper allowed to meet. There is no difficulty in making the bulbs thick enough to bear handling, and yet sufficiently thin to give way when required.

In the preceding remarks, I have chiefly referred to the difficulty experienced



in drying gases. But organic solids, such as litmus and colouring matter, though probably more readily dried than gases, are certainly with difficulty rendered anhydrous. The difficulty is too familiar to every chemist who has made organic analyses, to call for any illustration or proof. Reference has already been made to the desiccating power of currents of air, and to the likelihood of a solid being more effectually dried by a gas than a gas by a solid. If, however, it is impossible to supply a current of perfectly dry air, it may be doubted whether it is possible to render a solid anhydrous by passing air over it. It is difficult to imagine that air, containing *ex hypothesi* some moisture, should make a solid absolutely dry, drier than the air itself is; yet it is not impossible that it should. The tension which heat gives to water-vapour; its great dilatation when present in small quantity; and its diffusion through a large volume of gas, may more than balance any power on the part of the solid to attract or condense it. There may be a limit to condensation, as well as to vaporisation.

Notwithstanding all that has been urged in this section, in reference to the difficulty of rendering gases *absolutely* dry, it will not, I think, be questioned, that in the experiments I have recorded, a close approximation to actual dryness was attained in many of the trials. And, conceding that traces of moisture may have been present, I may, nevertheless, with some justice, argue, that if the removal of a certain amount of water from gases arrests for months their action on colours, *a fortiori*, the total abstraction of moisture would still more decisively negative that action.

VI. *On the Action on Dry Organic Colouring Matters of the liquefied Anhydrous Gases, and of Chlorine dissolved in liquids containing no Oxygen.*

The second series of experiments, as I have already mentioned, was made with the view of ascertaining in what way water acts, when it accelerates the action on colouring matter of the gases referred to, but particularly of chlorine. According to the prevailing theories of chemists, when water meets dry carbonic and sulphurous acid, or dry ammonia, it does not merely dissolve them, but allows its elements to be appropriated by each of these gases, which become, in consequence, compounds possessed of new relations to bases, acids, colouring matters, and the like. I shall therefore set these gases aside, as not admitting of direct comparison with chlorine, which chiefly concerns us. There is no reason, on the other hand, for supposing that water does more than merely dissolve oxygen, sulphuretted hydrogen, and hydrochloric acid, so that that liquid may be supposed to change their relation to colours in the same way as it does that of chlorine.

The older chemists held by the axiom, "*Corpora non agunt nisi soluta,*" and by means of it could fully have accounted for the difference in action on colours



of the dry and moist gases. In our own day, however, the problem takes a somewhat different shape, for we have learned to liquefy the gases without the intervention of a solvent. Three of the four gases last referred to, which simply dissolve in water, viz., chlorine, sulphurous acid, and sulphuretted hydrogen, admit of liquefaction, although quite anhydrous. It has been held, accordingly, that the liquefaction of a gas changes its properties, in the same way as dissolving it in water would.

With a view, so far at least, to examine this point, I exposed carefully dried blue litmus-paper to the action of liquid bromine (which is equivalent to a liquefied gas), repeatedly rectified from chloride of calcium, and supposed to be anhydrous. Ultimately the paper was quite bleached; but the decolorising action was slow, certainly much slower than that of hydrated bromine. Specimens accompany this paper. The dark colour, however, of that element makes it an unsatisfactory substance to work with, in relation to changes of tint in the bodies upon which it acts. From experiments such as I have described, as well as from theoretical observations, it has been inferred that the function of water in relation to the gases I have been considering is simply to effect their mediate liquefaction, and thereby to bring them into closer physical contact with the colouring matters than their elastic condition permits. So general a conclusion, however, as this, which would imply that a liquefied gas has the same properties as a dissolved one, is certainly in the meanwhile without proof, and is probably untenable. So far as they have been examined, the liquefied gases present properties very different from those exhibited by the same bodies when in aqueous solution, although their action on colouring matters has been less inquired into than might have been expected.

There is, moreover, this manifest distinction between the action on a colouring matter of a liquefied gas, and of an aqueously dissolved one, that in the former case the gas only is in the liquid form, the colouring matter remaining solid, whilst in the latter the water dissolves alike the colouring principle and the gas, and brings both into a condition far more favourable to chemical action than where the one only is liquid.

It is further certain that much must depend on the force of the adhesive attraction of the liquidised gas for the dry colour. A liquid which cannot wet a solid will exert little, perhaps no chemical action upon it, although it may produce a marked effect when both are dissolved in water.

Again, if the liquidised gas can dissolve the colouring matter, we may be certain that, sooner or later, it will affect it; but if it cannot dissolve it, the latter may be totally unaltered by its presence. The slow action of dry bromine is probably related, either to incapacity of quickly wetting, or of dissolving litmus; perhaps to both.

In connection with this subject, I tried an experiment with liquefied anhydrous



sulphurous acid, which yielded a result so interesting, that I mention it particularly. A piece of blue litmus-paper was exposed for three hours to a current of dry air, and then sealed up in the narrow tube in which it had been dried. The sealed bulb, containing the paper, was placed in a tube immersed in a mixture of pounded ice and salt, and carefully dried sulphurous acid transmitted through the arrangement. As soon as a sufficient quantity of the gas had assumed the liquid form, at the low temperature to which it was exposed, the open ends of the tube were sealed, and it was shaken till the bulb within broke, and allowed the paper and the liquefied gas to come in contact with each other. The paper was instantaneously soaked through, and completely wetted, but its blue colour remained totally unaltered, whilst an aqueous solution of sulphurous acid would have instantly reddened it. The liquidised gas acquired no colour itself, even after a fortnight's contact with the litmus-paper. It appeared to wet it without dissolving anything from it.

The retention of the blue tint on the part of the paper was, however, only temporary. In an hour and a quarter it had become dark purple, and the blue slowly faded, till, in twenty hours, the paper was bright red. No indication of bleaching action appeared.

I attribute the final reddening to the production of water, generated out of its elements in the litmus or paper, or both, by the influence of the sulphurous acid. For, if anhydrous liquid sulphurous acid possessed the power, *per se*, of reddening vegetable blues, there seems no reason why its action should be so long delayed, when it wetted the coloured paper so readily. And it could not owe its reddening power to water present in it, ready formed from the first, otherwise it would have reddened instantaneously.

I set aside, therefore, as at least unproven, and, further, as not probable, the dogma, that the mere passage of an elastic fluid, such as chlorine, from the state of gaseity to that of liquidity, is the whole cause of its accelerated action on colours, when dissolved in water. It seemed to me, indeed, that the acceleration of action was as much owing to the water liquefying the colouring matter as to its liquefying the gas, and that one might venture, in the spirit of the elder chemists' motto already quoted, to infer, that any liquid which dissolves alike the gas and the colouring matter, would be as efficacious as water in determining the destruction or modification of the colour. But, I have learned by experiment, that this also is too general a conclusion, and that it is quite possible for a liquid to dissolve simultaneously a colouring matter and a gas, and yet not exhibit the results which it would present if water were the solvent of both.

So far as this branch of the inquiry is concerned, I have been compelled, by want of leisure and opportunity, to limit myself almost entirely to chlorine. This gas is dissolved by chloroform, by bisulphuret of carbon, and by the volatile oils of the type of spirit of turpentine ( $C^3 H^4$ ). None of these liquids, when pure, contain



oxygen, and all of them dissolve several colouring matters. Yet, not only dry, but moist chlorine may be passed through solutions of the colouring principle of false alkanet root (*anchusa tinctoria*), in the solvents mentioned, without bleaching occurring.

On the other hand, solutions of blue litmus, in chloroform and bisulphuret of carbon, are bleached instantaneously by dry chlorine. I took the greatest precautions in these trials to exclude moisture. Paper was dispensed with. A solution of blue litmus was dried up in a glass tube, and desiccated in a current of air. The chloroform, or sulphuret of carbon, was repeatedly rectified over chloride of calcium, and finally distilled into a bulb communicating with the outer air, through a narrow tube filled with the same hygrometric salt. The bulb was then sealed, and placed within the tube containing the litmus at the commencement of the experiment. Chlorine was ultimately passed over the colouring matter for some minutes, in order to make certain that the gas was too dry to act unaided on the colour. The tube was then sealed, full of chlorine, and shaken till the bulb broke. The blue colour immediately disappeared, and the liquid became of a pale yellow tint.

The tincture of alkanet in chloroform or sulphuret of carbon retained its bright red colour, if kept in darkness; but less than an hour's exposure in the open air, though the sky was clouded, sufficed to turn the scale in favour of bleaching, and the colour disappeared.

From these results it appears that, contrary to DAVY's view, chlorine can bleach though oxygen be absent, for chloroform contains none; and that neither of the elements of water is essential to its bleaching action, for sulphuret of carbon is devoid of both. The further conclusion seems unavoidable, that neither water nor any other liquid is essential to the decolorising action of chlorine, otherwise than as enabling the gas and the colour to come within the sphere of chemical action, by dissolving both. This function, water probably performs better than any other liquid, in virtue of its solvent power for most substances exceeding that of almost all other fluids.

A similar conclusion, *mutatis mutandis*, may be extended to oxygen, sulphurous, hydrosulphuric, and hydrochloric acids, but with this qualification, that specific differences may be expected to occur with all the gases named, as to their action on any one colouring matter, and with different colouring matters, as to their deportment with any one of the gases.



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